^{13}C and ^{1}H Nuclear Magnetic Resonance Study of Solvent Effects on Tautomerism in 1-Aryl-3-methyltriazenes [1]

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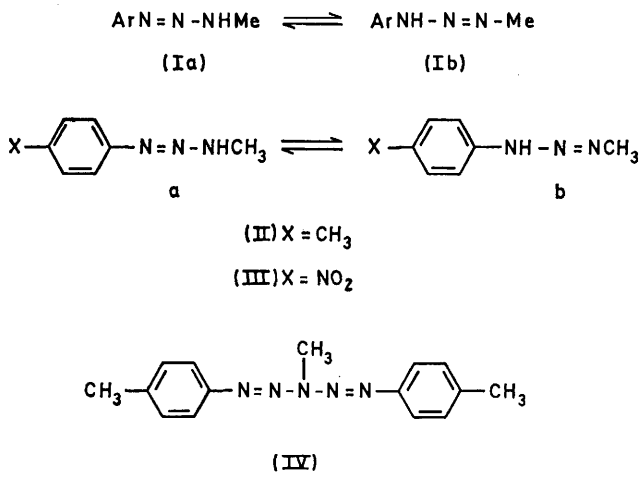
^{13}C and ^{1}H n.m.r. spectra of 1-*p*-tolyl- (II) and 1-*p*-nitrophenyl-3-methyltriazene (III) have been recorded in $CDCl_3$ at variable temperatures and in [$^{2}H_6$]DMSO solutions at ambient temperature. Assignment of ^{13}C and ^{1}H signals to one or both of the tautomeric species ($ArN{=}N{\cdot}NHCH_3$ or $ArNH{\cdot}N{=}NCH_3$) has been carried out with the aid of gated decoupling and full ^{1}H decoupling methods and by comparison of chemical shifts with those of the model compounds *p*-nitroaniline, 3,3-dimethyl-1-*p*-nitrophenyltriazene, and 3-methyl-1,5-di-(*p*-tolyl)-pentaza-1,4-diene (IV). The ^{13}C spectrum of (II) in $CDCl_3$ shows signals assigned to the conjugated tautomer (IIa), but not the unconjugated tautomer (IIb); additional signals in the ^{13}C spectrum of (II) are shown to arise from the pentazadiene (IV), which is present as an impurity (*ca.* 10%) in commercial samples of (II). ^{1}H and ^{13}C spectra of (IV) have been completely assigned. The tautomeric equilibrium (IIa) $\rightleftharpoons$ (IIb) is considerably slowed in [$^{2}H_6$]DMSO as solvent, so much so that two full sets of aromatic peaks are visible in the ^{13}C spectrum of (II) in [$^{2}H_6$]DMSO at room temperature and the ^{1}H spectrum clearly shows signals unequivocally assigned to the unconjugated tautomer (IIb). The equilibrium (IIa) $\rightleftharpoons$ (IIb) is shown to be concentration dependent. For $CDCl_3$ solutions of (II), resolution of ^{1}H signals due to the minor tautomer (IIb) is only possible in dilute solutions, and the ^{13}C signals of IIb are observed in the 62.8 MHz spectra of dilute solutions. For the first time, full ^{13}C spectra of both tautomers of the *p*-nitrophenyltriazene (IIIa) $\rightleftharpoons$ (IIIb) are observed at room temperature in [$^{2}H_6$]DMSO and the ^{1}H spectra of (III) in [$^{2}H_6$]DMSO or in $CDCl_3$ at room temperature also show the presence of both tautomers. The relative proportions of tautomers (IIIa) : (IIIb) was found to be 49 : 51 in [$^{2}H_6$]DMSO.

THE tautomeric equilibrium of 1-aryl-3-methyltriazenes (Ia) $\rightleftharpoons$ (Ib) has been extensively studied by i.r.[2] and n.m.r.[3-6] techniques. For the *p*-tolyl compound (II), which has been investigated in acetone,[3] methylene chloride,[4] and chloroform [5,6] solutions, there is little correlation among measurements for different solvents, and some disagreement between measurements in a single solvent. A third tautomer (ArNHNHN=CHR) is



also possible, and has been suggested [7] as an explanation of the electronic spectra and optical activity measurements on homologous monoalkyltriazenes. In the present work we have re-examined the ^{13}C and ^{1}H n.m.r. spectra in $CDCl_3$ solution, and as an aid in assessing these spectra we have recorded the spectra of some related compounds. Important to this work is the use of [$^{2}H_6$]DMSO as solvent. In this case, dramatic solvent effects on the equilibrium are observed and these solvent effects have led to rationalization of previous experimental measurements.

DISCUSSION

Curci and Lucchini [3] showed by ^{1}H n.m.r. of [$^{2}H_6$]acetone solutions of 3-methyl-1-*p*-tolyltriazene (II) that at ambient temperature, the tautomeric equilibrium was rapid on the n.m.r. time scale, with the NCH_3 signal a broad singlet at 27°. Cooling to −80° gives an NCH_3 doublet, δ 3.10, for the dominant (ΔH 1.1 ± 0.1 kcal mol^{-1}) conjugated form (IIa) and an NCH_3 singlet, δ 3.48, for the minor tautomer (IIb).

The ^{1}H n.m.r. spectra of solutions of (II) in methylene chloride [4] or $CDCl_3$ [5] give less straightforward results. In CH_2Cl_2 at −65°, (II) shows only a sharp doublet for NCH_3 and a well resolved quartet for NH. At 25° both peaks are broad and unresolved. In $CDCl_3$ solution at 25° a very sharp NCH_3 singlet is observed, with broadening as the temperature is lowered and the eventual appearance of a well resolved doublet at −40°. A single NH peak is observed over the temperature range −40 to +60°.

Two interpretations of these results have been proposed. Isaacs and Rannala [4] believed that there was a rapid equilibrium between a large concentration of the conjugated tautomer (IIa) and a small concentration of the unconjugated tautomer (IIb). If this were correct the reasonable implications would be either (a) the concentration of (IIb) is vanishingly small, or (b) the chemical shifts of all corresponding protons in the two tautomers are identical, or (c) the minor tautomer gives signals which are broadened by some additional phenomenon which is rapid even at the lowest temperature attainable. Vaughan [5] has summarized n.m.r. and i.r. evidence in support of the simpler hypothesis that only a single tautomer is present and that the broadening observed in room temperature spectra is the result of intermolecular exchange of molecules of this single tautomer.

Part of the answer is provided by ^{13}C n.m.r. spectra of $CDCl_3$ solutions of (II). Iwamura *et al.*[6] found no NCH_3 signal at room temperature and only two aromatic carbon signals. Cooling the solution to −36.5° gives the full set of peaks expected for a single tautomer and two additional peaks at δ 54.0 (weak) and 115.6 p.p.m. (weak, broad). From measurements on *o*-dichlorobenzene solutions of (II) and assuming coincidence of all four remaining peaks of (IIb) with those of (IIa), they estimated an 18% contribution of (IIb) at −36.5°.

To confirm the assignments of Iwamura *at al.*[6] and as a model for more complex triazenes we have recorded the ^{13}C spectrum of (II) in $CDCl_3$ under conditions of gated decoupling as well as of full ^1H decoupling. Table 1 compares our experimental results with those previously reported.

TABLE 1

Chemical shifts and assignments in the ^{13}C n.m.r. spectrum of 3-methyl-1-*p*-tolyltriazene (II) in $CDCl_3$

	Present work (room temperature) δ (p.p.m.)	Iwamura *et al.*[6] (−36.5°) δ (p.p.m.)
Tautomer (IIa)		
C–1	146.4	147.9
C–2	119.0 (br)	120.0 (br, exch.)
C–3	129.3	129.4 *
C–4	134.6	135.5
N–CH_3	32—36 (br)	31.2 (br)
C–CH_3	20.6	21.2 *
Tautomer (IIb)		
C–1		
C–2		115.6
C–3		129.4 *
C–4		
N–CH_3		54.0
C–CH_3		21.2 *
Pentazadiene (IV) [additional signals in spectrum of crude triazene (II)]		
C–1		
C–2	121.8	
C–3	129.5	
C–4	138.4	
N–CH_3	28.0	
C–CH_3	20.9	

* Coincidences.

The ^{13}C signals assigned to tautomer (IIa) are in very good agreement with the earlier result. The intense signal, δ 129.3 p.p.m., is correctly assigned to the carbons *meta* to the triazenyl substituent, giving in the gated decoupling experiment the splittings 152.1 Hz corresponding to directly bonded ^{13}C–H coupling, 11.2 Hz (doublet), and 5.0 Hz (quartet) as predicted by the first-order rules and as observed for other *p*-tolyl compounds. The *ortho*-carbon signal, δ 119.0 p.p.m., is so broadened that only the directly bonded splitting, 160 Hz, can be observed. The C–CH_3 signal, δ 20.6 p.p.m., gives the expected quartet, 126.3 Hz, of triplets, 3.9 Hz. The other peaks are so weak and/or broadened that gated decoupling patterns could not be determined.

Our ^{13}C spectra of commercial samples of (II) contain additional signals not previously reported: weak lines at δ 20.9, 28.0, and 138.4 and strong lines at 121.8 and 129.5 p.p.m. The pattern of these lines corresponds to a species with a *p*-tolyl ring system with a nitrogen substituent (reducing the ^{13}C intensity of the carbon bonded to it) and an additional NCH_3 peak; the chemical shifts do not correspond to *p*-toluidine and methylamine, the expected decomposition products of the triazene. The δ 28.0 p.p.m. peak is exactly one-half the intensity of the δ 20.9 p.p.m. peak, suggesting two CCH_3 and one NCH_3 per molecule. The ^1H spectrum of crude (II) shows an additional NCH_3 signal and a weak AA'BB' multiplet. These observations are in accord with the presence in commercial samples of (II) of *ca.* 10% of the pentazadiene (IV). In order to confirm this hypothesis and for use as a model compound we undertook the synthesis of pentazadiene (IV). A report by Terent'ev [8] suggests that recrystallization of methyltriazenes from light petroleum induces disproportionation, resulting in formation of the methylpentazadiene. In our hands, however, recrystallization of commercial 3-methyl-1-*p*-tolyltriazene did not produce additional pentazadiene but completely removed the 10% impurity present in the commercial material. The pentazadiene (IV) was prepared, but in low yield, according to the method of Dimroth,[9] by the diazotization of *p*-toluidine, followed by reaction with a one-half molar equivalent of methylamine.

The ^1H n.m.r. spectrum of the product pentazadiene in $CDCl_3$ solution shows δ 2.36 (6 H, s, CCH_3), 3.77 (3 H, s, NCH_3), and 7.1—7.7 (8 H, AA'BB', *p*-substituted aromatic). The highfield half of the AA'BB' multiplet is broadened by coupling to the methyl group of the *p*-tolyl ring, the signal of the CCH_3 group being similarly broadened by the coupling. Irradiation at δ 2.36 gave the normal sharp lines of the AA'BB' multiplet, whilst decoupling at δ 7.20 gave a considerably sharper CCH_3 peak. The ^{13}C signals (and the off-resonance multiplicities) of the pentazadiene are δ 21.0(q), 28.0(q), 121.9(d), 129.5(d), 138.4(s), and 146.5(s) p.p.m., which are very similar to the chemical shifts assigned for the conjugated tautomer of *p*-tolylmethyltriazene and exactly coincident with the impurity peaks in $CDCl_3$ solutions of commercial (II), *i.e.* δ 20.9, 28.0, 121.8, 129.5, and 138.4 p.p.m. The ^{13}C signals of the pentazadiene were fully assigned by a gated decoupling experiment and the result may be compared with that of the similar assignment for tautomer (IIa): δ 21.0 p.p.m., for CCH_3, becomes a quartet, 126.6 Hz, of triplets, 4.1 Hz; δ 28.0 p.p.m. shows only the quartet 142.6 Hz, expected for an isolated NCH_3 group; δ 121.9 p.p.m., the signal for the carbons *meta* to CCH_3 is a doublet, 161.5 Hz, of doublets, 5.4 Hz; δ 129.5 p.p.m., for the carbons *ortho* to CCH_3, gives an almost first-order pattern: 158.3 (doublet), 6.3 (doublet), 5.1 (quartet) Hz. The quaternary carbons were assigned by comparison of chemical shifts with those observed for the triazene.

The question of the equilibrium (IIa) $\rightleftharpoons$ (IIb) for $CDCl_3$ solutions was not satisfactorily resolved in these experiments. The situation was not improved by recording 62.8 MHz ^{13}C spectra of a nearly saturated

solution of (II) in $CDCl_3$ at temperatures as low as −60°. At −60° the full set of signals assigned to (IIa) are relatively sharp; however, the δ 115 p.p.m. peak assigned to (IIb) is still broad. Furthermore, there is no signal at δ 54 p.p.m. in the 62.8 MHz spectrum.

Several factors may be contributing to the difficulty of detecting the signals from tautomer (IIb) in the experimental results reported for (II). The *p*-CH_3 substituent may produce only small chemical shift differences between (IIa and b). Alternatively the *p*-CH_3 group may increase the rate of tautomeric equilibrium. The differences reported between the chemical shifts in [$^2H_6$]acetone solution and $CDCl_3$ solution may simply be a reflection of the variation in hydrogen-bond acceptor ability of the solvents. We determined to study these possible contributions by a combined strategy of variations of the solvent system and of the substituent in the *para*-position of the aryl group.

The ^{13}C spectrum of 3-methyl-1-*p*-nitrophenyltriazene (III) in [$^2H_6$]DMSO provides the first example where full spectra are observed at room temperature for both tautomers. These spectra were assigned by comparison of peak heights, off resonance multiplicities, and chemical shifts with those of the model compounds, 3,3-dimethyl-1-*p*-nitrophenyltriazene and *p*-nitroaniline. The *p*-nitroaniline spectrum was assigned by comparing observed chemical shifts with those calculated from tabulated substituent effects, and confirmed by the spectrum recorded under conditions of gated decoupling.

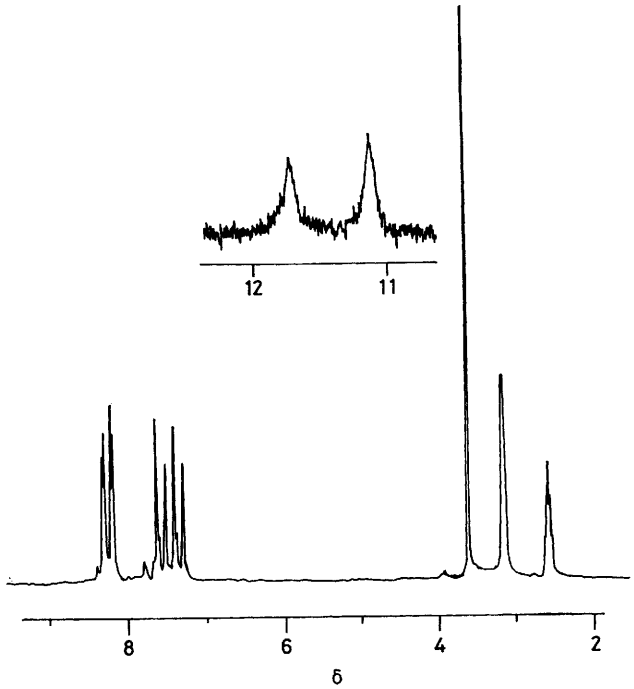


FIGURE 1 ^1H N.m.r. spectrum of 1-*p*-nitrophenyl-3-methyltriazene (III) in [$^2H_6$]DMSO at 37°

Even in $CDCl_3$ solution, intermolecular exchange is much slower for both tautomers of (III) than for the corresponding tautomers of (II), so much so that this is the first case where the room temperature ^1H spectrum shows the presence of both tautomeric forms and their presence is confirmed at lower temperatures (Figure 2). At −50° the high field signal at δ 3.21 becomes a doublet (J 6.04 Hz) and the low field NCH_3 signal at δ 3.62 becomes a sharp singlet. Similarly the high field half of the AA'BB' multiplet splits to two sets, one centred at δ 7.2 for the unconjugated tautomer, the other at δ 7.5 for the conjugated tautomer. This assignment was confirmed by the low temperature spectrum of a solution in [$^2H_6$]acetone. The pattern centred on δ 7.2 broadens significantly at low temperatures as a result of the vicinal coupling to the NH proton of the unconjugated tautomer. Thus compound (III) exhibits the behaviour expected for a simple tautomeric equilibrium.

TABLE 2

Chemical shifts, multiplicities, and assignments in the ^{13}C spectrum of 3-methyl-1-*p*-nitrophenyltriazene (III) in [$^2H_6$]DMSO, compared with the model compounds *p*-nitroaniline and 3,3-dimethyl-1-*p*-nitrophenyltriazene

	p-$O_2NC_6H_4N$=NNHCH$_3$ (IIIa)					*p*-$O_2NC_6H_4NHN$=NCH_3(IIIb)				
	C-1	C-2	C-3	C-4	NCH_3	C-1	C-2	C-3	C-4	NCH_3
(III)	148.81 (s)	120.48 (d)	124.70 (d)	144.01 (s)	30.7 (q)	140.74 (s)	112.86 (d)	125.95 (d)	156.25 (s)	47.57 (q)
$O_2NC_6H_4N$=$NN(CH_3)_2$	155.84 (s)	120.34 (d)	124.51 (d)	144.38 (s)						
$O_2NC_6H_4NH_2$						135.94 (d)	112.46 (d)	126.28 (d)	155.62 (q)	

The agreement between the chemical shifts of the triazene tautomers and those of the appropriate model compounds is remarkably good (Table 2). The only cases where a discrepancy of >1 p.p.m. is found are for C-1 of the conjugated tautomer and C-4 of the other tautomer. The carbon directly bonded to a substituent is, of course, highly susceptible to slight variations in the substituent, whilst the substituent effect of an amino- or substituted amino-group on the chemical shift of a *para*-carbon is both large and subject to considerable change as the *N*-substitution pattern changes.

The ^1H spectrum of (III) in [$^2H_6$]DMSO at room temperature (Figure 1) also shows the presence of both tautomers; chemical shifts of the NCH_3 protons are δ 3.57 for the unconjugated and δ 3.14 for the conjugated tautomers, with the integrations showing the unconjugated form to be in slight excess (51 : 49).

The effect on the spectra of using [$^2H_6$]DMSO as solvent for (II) proved to be dramatic. Figure 3, the

^{1}H n.m.r. spectrum of (II) in [$^2H_6$]DMSO at room temperature, shows full sets of signals for both tautomers (IIa and b), very similar to the results for [$^2H_6$]acetone

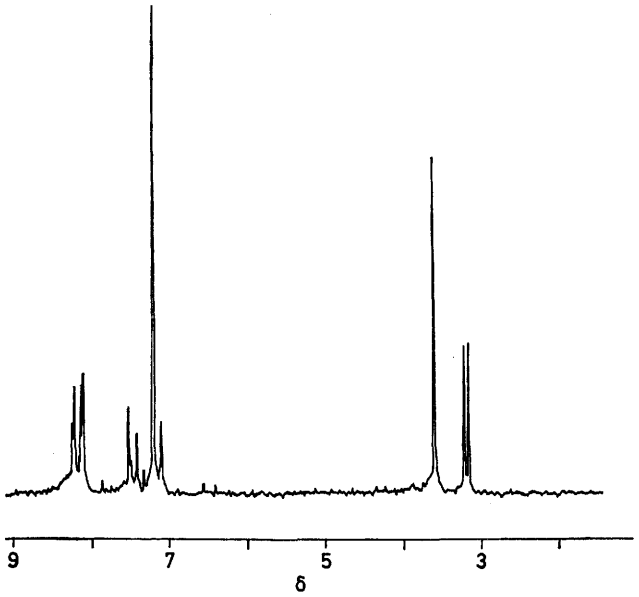


FIGURE 2 ^{1}H N.m.r. spectrum of 1-*p*-nitrophenyl-3-methyltriazene in deuteriochloroform at −60°

solutions at low temperature. Table 3 compares the ^{13}C chemical shifts of (II) in [$^2H_6$]DMSO with the low temperature $CDCl_3$ solution spectra; [$^2H_6$]DMSO separates the signals of (IIa and b) but only by relatively

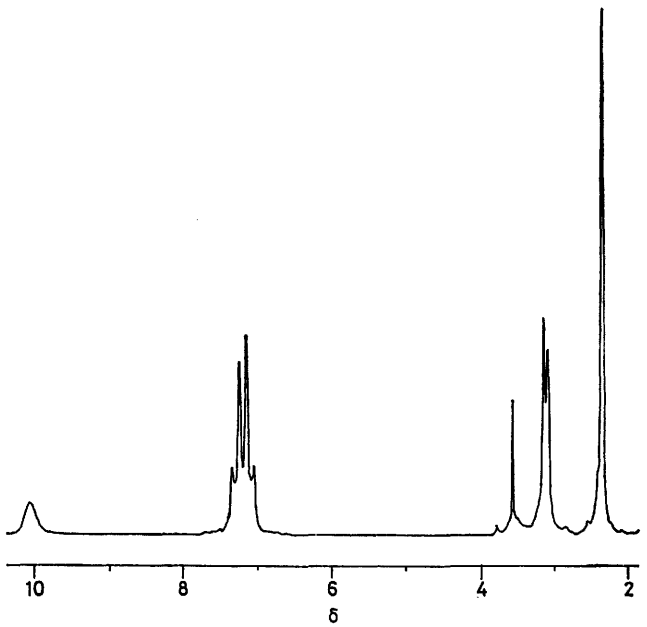


FIGURE 3 ^{1}H N.m.r. spectrum of 1-*p*-tolyl-3-methyltriazene (II) in [$^2H_6$]DMSO at 37°

small amounts for the *ortho*- and *meta*-carbons [shifted by 1.5 and 0.5 p.p.m.; *cf.* 7.6 and 1.2 p.p.m. for (III)]. In view of this observation the coincidence of a number of ^{13}C signals in $CDCl_3$ solution is reasonable.

The slowing of the equilibrium (IIa) ⇌ (IIb) on going from [$^2H_6$]acetone to [$^2H_6$]DMSO as solvent suggests that intermolecular exchange may be an important contributor to the tautomeric change, with slower exchange when the NH protons are hydrogen bonded to the strong acceptor DMSO, more rapid exchange in the weaker acceptor acetone, and perhaps very rapid exchange in $CDCl_3$.

If this were the case, it would be expected that the spectra should be concentration dependent, as reported for the tautomeric equilibrium of 1,3-dimethyltriazene,[10] in which case high solute concentration increases

TABLE 3

Chemical shifts and assignments in the ^{13}C n.m.r. spectrum of 3-methyl-1-*p*-tolyltriazene in [$^2H_6$]DMSO (present work) [b] compared to $CDCl_3$ spectra reported by Iwamura *et al.* (ref. 6) [a]

	p-$CH_3C_6H_4N{=}NNHCH_3$ (IIa)		*p*-$CH_3C_6H_4NHN{=}NCH_3$ (IIb)	
	$CDCl_3$ [a]	[$^2H_6$]DMSO [b]	$CDCl_3$ [a]	[$^2H_6$]DMSO [b]
CCH_3	21.2 *	20.48 *	21.2 *	20.48 *
NCH_3	31.2	30.30	54.0	
C–1	147.9	148.70		146.20
C–2	120.0	120.13	115.6	121.67
C–3	129.4 *	129.31	129.4 *	129.85
C–4	135.5	134.25		138.49

* Coincidences.

the rate of tautomeric interchange. For solutions of (II) in [$^2H_6$]DMSO this is certainly true: the δ 3.4 signal for the NCH_3 group of (IIb) is so broadened as to be barely observable for a saturated (*ca.* 40%) solution, but to be a sharp singlet for a 1% solution. The effect of changing concentration on the signals of (IIa) is much less than for the weaker signals of (IIb). The ^{13}C spectrum of a [$^2H_6$]DMSO solution of (II) reported in Table 3 does not include a NCH_3 peak for (IIb). Presumably, it, too, is broadened by the postulated exchange.

We were considerably surprised to observe ^{1}H signals of both tautomers of (II) in $CDCl_3$ solution at low temperature. Figure 4 compares spectra of 11 and 22% solutions of (II) in $CDCl_3$. The improved resolution of signals in the more dilute solution is evident, as is the relatively greater broadening of the (IIb) NCH_3 peak in the spectrum of the more concentrated solution. Presumably the previously reported continuous wave ^{1}H spectra like the ^{13}C spectra were recorded for moderately concentrated solutions, and thus the (IIb) signals were broadened by rapid exchange.

A single 62.8 MHz ^{13}C spectrum at −60° of a 5% solution of (II) in $CDCl_3$ was provided to us. This shows the previous result of sharp signals for (IIa) and, in addition, a narrow signal at δ 115.1 p.p.m. However, this δ 115.1 p.p.m. peak represents only *ca.* 5% of the intensity of (IIa), with the rest of the (IIb) intensity in a peak at δ 112.9 p.p.m. For the NCH_3 region peaks at δ 48.4 and 34.6 p.p.m. are observed. No peak at δ 54.0 p.p.m. is seen in this spectrum. It is tempting to speculate that the division of the (IIb) signals arises

from hindered rotation about the N–N single bond of (IIb); however, we have shown that the previous apparently anomalous results arise from solvent effects

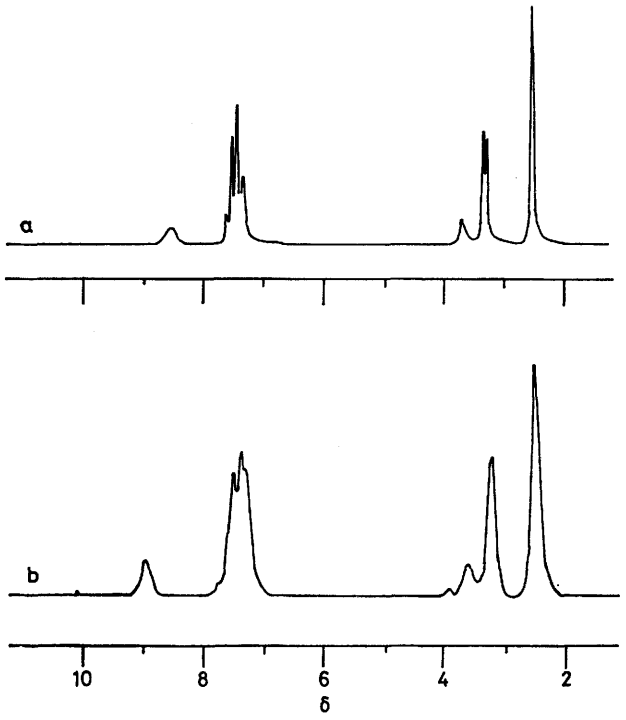


FIGURE 4 ^{1}H N.m.r. spectra of 1-*p*-tolyl-3-methyltriazene (II) for concentrations (a) 11%, and (b) 22%, in $CDCl_3$ at 37°

and it is not reasonable to postulate additional effects on the basis of a single spectrum.

EXPERIMENTAL

The 20 MHz ^{13}C and 80 MHz n.m.r. spectra were recorded on a Varian CFT-20 spectrometer. The chemical shifts are reported with respect to tetramethylsilane, although the ^{13}C shifts were measured with respect to the ^{13}C shifts of the appropriate solvent and calculated from tabulated values of these shifts. The 62.8 MHz ^{13}C n.m.r. spectra were recorded on a Bruker WM250 n.m.r. spectrometer.

Materials.—3-Methyl-1-*p*-tolyltriazene (II) was obtained commercially from Aldrich Chemical Co., and was purified by recrystallization from light petroleum (b.p. 60—80°); the pure triazene had m.p. 80—82° (lit.,[11] 81.5°). 3-Methyl-1-*p*-nitrophenyltriazene (III) was obtained by the reported method; [12] 3,3-dimethyl-1-*p*-nitrophenyltriazene was obtained by coupling dimethylamine with *p*-nitrobenzenediazonium chloride and had m.p. 148—150° (orange plates) (lit.,[13] 144—145°). *p*-Nitroaniline was obtained commercially in pure form.

3-*Methyl*-1,5-*di*-(p-*tolyl*)-*pentaza*-1,4-*diene* (IV).—*p*-Toluidine was diazotized in hydrochloric acid and the diazonium salt solution was treated with half the molar equivalent of methylamine (40% aqueous solution). The mixture was basified with dilute sodium hydroxide and filtered to give an orange-red solid, which was washed with ethanol, filtered, and recrystallised from ethanol to give the pentazadiene, m.p. 147—148° (yellow prisms) (lit.,[14] 147°), δ($CDCl_3$) 2.36 (6 H, s), 3.77 (3 H, s), and 7.1—7.7 (8 H, m).

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