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174. A ^{13}C- and ^{15}N-NMR. Study of Some 1-Aryl-3,3-dimethyl Triazene Derivatives

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Summary. ^{13}C- and ^{15}N-NMR. spectra have been measured for a series of triazenes. The results are compatible with the significant contribution of a structure such as II. One-bond nitrogen-nitrogen coupling constants are reported.

There is a relatively widespread distribution of molecules containing nitrogen in which this heteroatom is involved in an extended π-system. In these cases it is possible that there is a considerable delocalization of charge density from (or to) the nitrogen from other atoms in the system. Triazenes of type **1** represent one such class of molecules. For a wide variety of X-groups, a dipolar structure, such as **2**, is thought [1] to be important. Indeed, variable temperature ^{1}H-NMR. studies have already demonstrated [1] that restricted rotation exists about the N(2)–N(3) 'single' bond. While ^{1}H-NMR. has shown that the methyl groups of **1** are not equivalent it is interesting to ask whether or not this non-equivalence stems only from **2** or whether a structure such as **3** makes a major contribution since, in both structures, alkyl groups on the amino-nitrogen would lie in magnetically non-equivalent sites. Since **3** implies a change in the nature of the carbon π-system, whereas **2** results primarily from changes at the nitrogen centers, a combined ^{13}C- and ^{15}N-NMR. study should be valuable as both of these forms of magnetic resonance are capable of monitoring changes in charge density at the nuclear center. To further this end we have synthesized and measured the ^{15}N-(I = 1/2, natural abundance = 0.36%) and ^{13}C-NMR. characteristics of two series of such triazenes with one set containing ^{15}N (greater than 95 atom % ^{15}N) at positions N(1) and N(2) and a second set enriched at positions N(2) and N(3).

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Experimental Part. – ^{15}N-NMR. spectra were recorded as $CDCl_3$ solutions at 9.12 MHz. Natural abundance ^{13}C-NMR. spectra were recorded as $CDCl_3$ solutions containing the natural abundance of both nitrogen isotopes. Both nuclei were measured using a *Bruker* HX-90 spectrometer operating in *Fourier* transform mode under conditions of complete proton decoupling. ^{13}C chemical shifts are reported relative to TMS whereas the ^{15}N resonances are relative to an acidified saturated solution of $^{15}NH_4Cl$.

The dimethylamine hydrochloride, aniline, sodium nitrite and ammonium chloride used in the synthesis of compounds described in this paper were enriched to the extent of 95 atom % and obtained from *Stohler Isotope Chemicals*, Rutherford, N.J. All of the double labeled triazenes used in this investigation were prepared by coupling dimethylamine with the appropriately labeled phenyldiazonium ion [2]. The method detailed by *Axenrod et al.* [3] was used to prepare the starting anilines. Isotopically labeled dimethyl amine and sodium nitrite were used for the synthesis of the other triazene derivatives. The following procedure is typical.

1-(p-nitrophenyl)-3,3-dimethyl-1,2-[^{15}N,^{15}N]-triazene. *p*-Nitro[^{15}N]aniline (95% ^{15}N, 0.1391 g; 0.001 mol) in 1.6 ml of 6M hydrochloric acid was diazotized at –5–0° with sodium nitrite (95% ^{15}N, 0.0713 g, 0.00103 mol) dissolved in 1 ml of water. To the clear diazonium solution was added 1 ml of an ice cold aqueous solution of dimethyl amine hydrochloride (0.0825 g, 0.00101 mol). The mixture was then made alkaline by dropwise addition of ice cold sodium hydroxide (25%) solution. The mixture was stirred at –5–0° for 1 h and the resulting yellow precipitate filtered off, washed with water, and dried. Yield: 0.1709 g (0.00088 mol, 88%) of product melting at 143–144° (lit. [4] m.p. 144–145°).

Results and Discussion. – Under conditions of complete proton decoupling, the ^{15}N- and ^{13}C-NMR. spectra of these molecules are relatively simple. Typical examples are shown in Figs. 1 and 2 for the 1-(4-chlorophenyl)-3,3-dimethyl, and 1-(4-methoxyphenyl)-3,3-dimethylhydrazines respectively, with the separations of the doublets shown in Fig. 1 representing the value $^{1}J(^{15}N,^{15}N)$. The ^{15}N and ^{13}C chemical shifts are shown in Tables 1 and 2 respectively, whereas the values $^{1}J(^{15}N,^{15}N)$ are shown in Table 3.

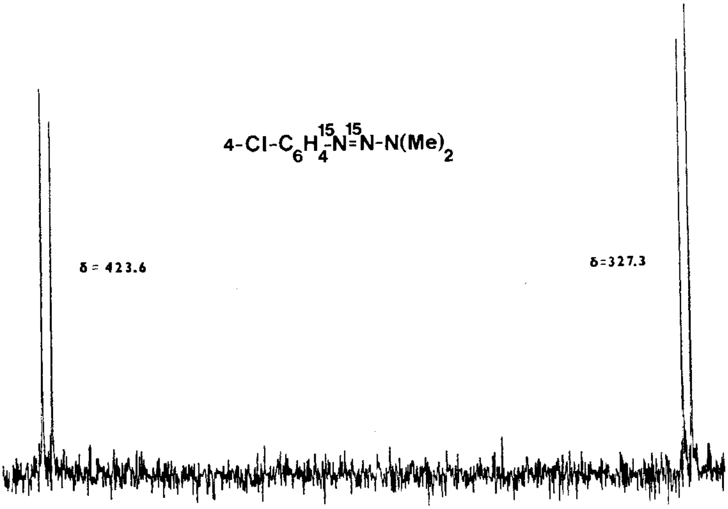


Fig. 1 $^{15}N\{^{1}H\}$-*NMR. spectrum of* $4\text{-}Cl\text{-}C_6H_4\text{-}^{15}N\text{–}N(CH_3)_2$

As may be seen from Table 1 the ^{15}N chemical shifts of N(1) and N(3) are most responsive to a change in the nature of the *para*-substituent X. Increasing the electron

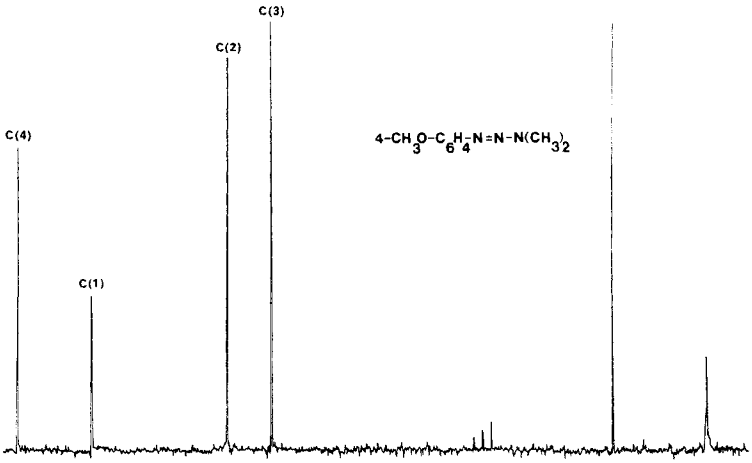
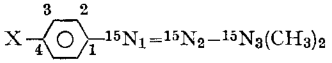


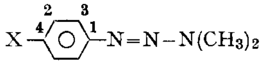
Fig. 2. *$^{13}C\{^1H\}$-NMR. spectrum of 4-MeO-C_6H_4-N=N-N$(CH_3)_2$*

Table 1. *^{15}N chemical shifts* [a]) *in 1-aryl-3,3-dimethyltriazenes*

			
X	N(1)	N(2)	N(3)
NO_2	320.0	428.0	138.0
Cl	327.3	423.6	128.9
H	332.1	424.1	127.3
OCH_3		421.1	124.4

[a]) Chemical shifts are relative to a saturated solution of $^{15}NH_4Cl$ and are considered to be ± 0.1 ppm. Data are for $CDCl_3$ solutions.

Table 2. *^{13}C chemical shifts* [a]) *in 1-aryl-3,3-dimethyltriazenes*

							
X	C(1)	C(2)	C(3)	C(4)	CH_3		other
NO_2	155.5	120.2	124.4	144.0	36.2	43.4	
Cl	149.1	121.4	128.4	129.9	39.0	(broad)	
H	150.7	120.3	128.6	125.2	38.8	39.1	
OCH_3	144.1	120.9	113.4	156.9	38.7		OCH_3 = 54.9

[a]) Chemical shifts are relative to TMS and are considered to be accurate to ± 0.1 ppm. Data are for $CDCl_3$ solutions.

withdrawing ability of X results in a deshielding of N(3) and a shielding of N(1) in keeping with a structure such as **2** which places negative charge on N(1) at the expense of N(3). Plots of the nitrogen shifts at both of these positions against the *Hammett* σ_p constant, are reasonably linear (see Fig. 3). The observation that,

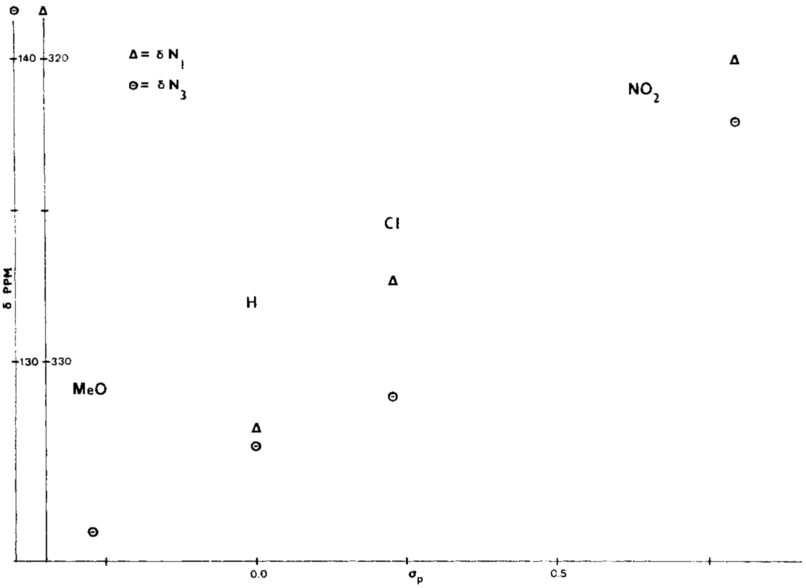
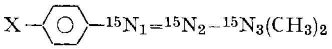


Fig. 3. *Plot of $\delta^{15}N$ vs. σ_p for the aryl triazenes*

Table 3. $^1J(^{15}N,^{15}N)$ [a]) *in the triazenes*



X	$^1J(N_1N_2)$	$^1J(N_2N_3)$
NO_2	12.8	13.4
Cl	12.8	13.4
H	12.8	14.0
OCH_3	12.2	14.0

[a]) Values are ± 0.7 Hz. Measured as $CDCl_3$ solutions.

qualitatively, the shielding of N(1) ($N(1)_{NO_2} - N(1)_H = 12.1$ ppm) is similar to the deshielding of N(3) ($N(3)_{NO_2} - N(3)_H = 10.7$ ppm) suggests that a structure such as **2** plays a role. The position of the amine nitrogen atom N(3) at considerably lower field than that of either $(CH_3)_2NH$ (– 25 ppm [5]) or 1,1-dimethyl hydrazine (+ 27 ppm [6]) more strongly suggests that this nitrogen is involved in the adjacent π-system[2]). Similar ^{15}N chemical shifts have been found for the aniline nitrogen of some phenylhydrazones (120–130 ppm [8]) where some overlap of the aniline lone pair to form an extended π-system is to be expected. In addition, the nitrogen chemical shift of N(1) appears at much higher field (320–340 ppm) than is to be expected for an azo-nitrogen atom (> 420 ppm) [7] [9], which could reflect some decrease in the double bond character at this center. The resonance position of N(2) is not especially unusual.

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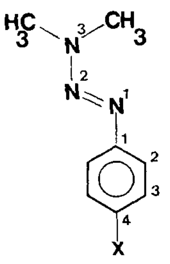
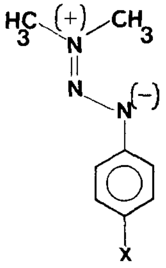
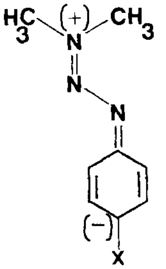
[2]) For consistency we have used $H^{15}NO_3$ as 343 ppm from $^{15}NH_4Cl$ since this value stems from the same laboratory [7] as does δ ^{15}N for dimethyl amine and unsymmetrical dimethyl hydrazine. Differences due to referencing will not effect our conclusions.



1



2



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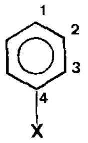

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To decide whether a structure such as **3** makes a significant contribution it is useful to evaluate the changes in the ^{13}C chemical shift of the *para*-carbon atom (C(4)) as X is varied. The shift in the position of this resonance will, in part, be responsive to changes in the resonance interaction of the $N{=}N{-}N(CH_3)_2$ group with the benzene ring. If one accepts the suggestion [10] that ^{13}C substituent effects in benzene rings are additive³) then a comparison of the effect of X on the C(4) position of **1** with the effect of X at C(4) in the simple benzene derivatives **4** is illuminating. Substitution of the groups NO_2, Cl and OCH_3 at C(4) of the triazene results in changes (all downfield) of 18.8, 4.7 and 31.7 ppm, respectively; whereas the changes in C(1) in the simple aromatics are 19.6, 6.4 and 31.4 ppm respectively [11]. Thus for $X = NO_2$ and Cl the *para*-carbon atoms in the triazene derivatives are shifted slightly less downfield than in the mono-substituted benzenes counterparts, whereas the methoxy derivative is shifted slightly further to lower field. These data are in keeping with the expectation that for the two electron withdrawing substituents, the $-N{=}N{-}N(CH_3)_2$ group will be a somewhat more effective donor to the aromatic moiety while the OCH_3 will be slightly less effective, relative to $X = H$. The $-N{=}N{-}N(CH_3)_2$ group itself is slightly electron donating in the parent triazine (C(4) for X=H is 125.2 ppm; $C_6H_6 = 128.5$ ppm).

Considering the ^{13}C chemical shift data there would seem to be some evidence for a structure such as III, although, in view of the relatively small changes from the

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³) This approach has been criticized, see *J. Bromilov, R. T. C. Brownlee, R. D. Topsom & R. W. Taft*, J. Amer. chem. Soc. *98*, 2020 (1976).

'normal' position of C(4'), it would seem unlikely that this form is a major contributor to the total structure. On the other hand the major changes in the positions of both N(1) and N(3) (80–100 ppm relative to our models) indicate that II should be thought of as the most important component in the molecular composite.

Part of the motivation for this work stemmed from the opportunity, provided by the multiple enrichment, to systematically measure the one bond homonuclear nitrogen coupling. A recent review [12] has pointed out that, with scattered exceptions, studies concerned with the magnitude of the values $^1J(^{15}N,^{15}N)$ are lacking. Values of 13.7 [13] and 19 Hz [14] have been reported for *trans*-azoxybenzene and dibenzylnitrosamine, respectively. Recently [15], a titanium complex containing unsymmetrically complexed molecular nitrogen showed $^1J(^{15}N,^{15}N) = 7$ Hz. As may be seen from Table 3 the one bond nitrogen-nitrogen coupling constants fall in the rather narrow range 12–14 Hz. Since the differences in these values approach the experimental error we can draw no conclusions from these data with regard to the bond order between N(1)–N(2) on the one hand and N(2)–N(3) on the other; however, we are able to add that we have observed both larger ($Ph_2{}^{15}N{-}^{15}NO = 22$ Hz) and smaller ($Me_2{}^{15}N{-}^{15}NO_2 = 4.9$ Hz) values for this type of coupling. These and other ^{15}N-NMR. data will be reported separately.

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