chromatography (eluting with 10% ether/1% acetic acid/hexane) gave 114 mg (76%) of the acid **7**, $n = 4$: IR 1710 cm^{-1} (CO_2H); UV 272, 283 nm (ϵ 47 700 and 37 400); ^1H NMR (300 MHz) was identical with the spectrum of **6**, $n = 4$, except the CO_2CH_3 signal was missing and the triplet for H-2 was at 2.39 ppm.

Anal. Calcd for $C_{20}H_{32}O_3$: C, 74.96; H, 10.06. Found: C, 74.68; H, 10.21.

Registry No. **1** (n = 3), 55444-67-2; **1** (n = 4), 87307-20-8; **2** (n = 4), 87307-21-9; **3** (n = 4), 87307-22-0; **4** (n = 4), 87307-23-1; **5** (n = 4), 87307-24-2; **6** (n = 4), 87307-25-3; **7** (n = 3), 87307-26-4; **7** (n = 4), 87307-27-5.

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^{15}N Nuclear Magnetic Resonance Spectroscopy of 1-Phenyl-3,3-pentamethylenetriazenes

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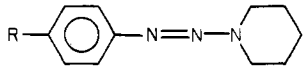
The π-conjugated nitrogen system of 1-phenyl-3,3-dialkyltriazenes is extremely stable against loss of nitrogen, and on reaction with acidic reagents the triazene system is converted to aryldiazonium salts. These combined properties of aryltriazenes are largely responsible for the increased use of aryltriazenes in synthetic and radiopharmaceutical chemistry.[1-5] The value of aryltriazenes in preparative chemistry and their interesting linear π-conjugated nitrogen system led us to investigate in some detail the ^{15}N nuclear magnetic resonance spectroscopy of the 1-phenyl-3,3-pentamethylenetriazene (**1**) system.

The use of ^{15}N nuclear magnetic resonance spectroscopy as a tool for studying the electronic structure of nitrogenous systems is well-known.[6] In 1976, Pregosin et al. made a preliminary study of three aryltriazene systems, using both ^{15}N and ^{13}C NMR spectroscopy, and concluded that aryltriazenes have dipolar character.[7] We now report a detailed study of the effect of polar substituents on the ^{15}N NMR chemical shifts of **1** and discuss the electronic structure of the aryltriazenes.



1

The ^{15}N NMR spectra of **1**, as exemplified by the spectrum of 1-phenyl-3,3-pentamethylenetriazene shown in Figure 1, are relatively simple, showing three distinct chemical shifts. The signal at δ −16.98 is assigned to N(1) by comparison with the spectrum of a sample enriched with N-15 in the 1-position. The signal at δ −206.33 is assigned to N(3) because it is sensitive to the type of secondary amino substituent. Thus, a change from a pentamethylenetriazene to a (diethylamino)triazene causes a chemical shift change of 4.5 ppm at N(3), while the other nitrogen resonances are little affected. The resonance at δ 73.54 is the only remaining signal, and it is therefore assigned to N(2).

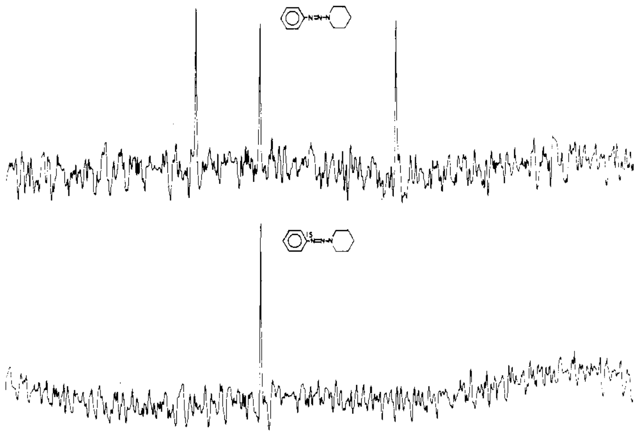
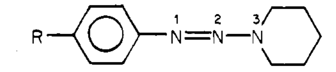


Figure 1. Upper spectrum: ^{15}N NMR spectrum of **1** at natural abundance (40% w/v, 43 000 scans). Lower spectrum: ^{15}N NMR spectrum of **1** with ^{15}N enrichment at N(1) (95% enrichment, 5% w/v, 23 000 scans).

Table I. ^{15}N NMR Chemical Shifts[a]

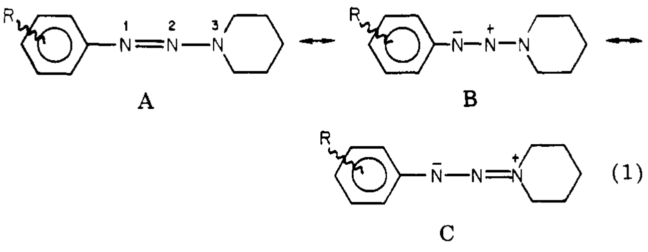


R	σ^b	$\delta_{N(1)}$	$\delta_{N(2)}$	$\delta_{N(3)}$
CH_3O	−0.268	−12.90	72.25	−208.81
CH_3CH_2O	−0.244	−13.33	72.4	−209.67
CH3	−0.17	−13.76	73.34	−207.52
H	0	−16.98	73.54	−206.23
F	0.062	−18.49	73.55	−206.45
Cl	0.227	−21.72	73.98	−204.30
Br	0.232	−21.29	74.41	−203.87
CH_3CO	0.50	−26.45	75.27	−200.00
CN	0.66	−30.11	76.17	−197.2
NO_2	0.78	−32.90	76.56	−194.62

[a] Relative to external $NH_4{}^{15}NO_3$. Positive numbers are ppm dowfield from the standard. [b] Values taken from Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 145.

The occurrence of N(3) upfield from N(1) and N(2) is consistent with the amine-like character of N(3). However, the triazene amine resonance of N(3) is approximately 50-ppm downfield from an isolated amine resonance. In addition, the azo resonances of N(1) and N(2) of the triazene are approximately 45-ppm upfield from that observed for isolated azo systems. These results qualitatively show the presence of a π-conjugated interaction for the entire triazene system.

The effect of the polar substituents on the nitrogen chemical shifts are discussed with reference to structures A–C in eq 1.



(1)

All of the nitrogen chemical shifts give an exceptionally good linear correlation with the polar Hammett σ values as shown in Figure 2 and Table I. N(1) shows the largest

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(1) (a) Tewson, T. J.; Raichle, M. E.; Welch, M. J. *Brain Res.* **1980**, *192*, 291. (b) Tewson, T. J.; Welch, M. J. *J. Chem. Soc., Chem. Commun.* **1979**, 1149.

(2) Ng, J. S.; Katzenellenbogen, J. A.; Kilbourn, M. R. *J. Org. Chem.* **1981**, *46*, 2520.

(3) Widdowson, D. A.; Rosenfeld, M. N. *J. Chem. Soc., Chem. Commun.* **1979**, 914.

(4) Ku, H.; Barrio, J. R. *J. Org. Chem.* **1981**, *46*, 5239.

(5) Wallach, O. *Justus Liebigs Ann. Chem.* **1881**, *235*, 242, 255.

(6) Levy, G. C.; Lichter, R. L. "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy"; Wiley: New York, 1979; p 167.

(7) Axenrod, T.; Mangiaracina, P.; Pregosin, P. S. *Helv. Chim. Acta* **1976**, *59*, 1655.

0022-3263/83/1948-4415$01.50/0

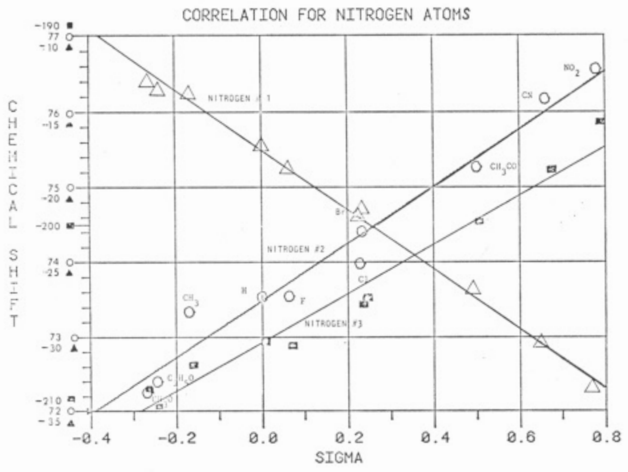

Figure 2. Correlation of N-15 chemical shifts with Hammett σ constants for aryltriazenes: (○) chemical shift for nitrogen atom 2 ($r = 0.979$), (△) chemical shift for nitrogen atom 1 ($r = 0.998$), (■) chemical shift for nitrogen atom 3 ($r = 0.986$).

sensitivity in chemical shift change with the substituent effect, with an overall chemical shift range of 20 ppm on going from methoxy to nitro substituents. The increased shielding of N(1) with increasing substituent electronegativity is consistent with stabilization of the negative charge on N(1) by the substituent in resonance structures B and C. Both N(2) and N(3) are deshielded as the substituent electronegativity increases, as would be expected for nitrogen atoms with positive character as shown for structures B and C in eq 1. The relatively small overall sensitivity (4.2 ppm) of the chemical shifts of N(2) to the substituent effects means that structure B is a minor contributing structure relative to A and C. The N(3) resonance, on the other hand, shows a large chemical shift sensitivity (14.2 ppm), which indicates that structure C is a major contributing member of the conjugated system.

The chemical shift results presented here for N(1), N(2), and N(3) of the triazene system 1, and the polar substituent effects on these shifts, are entirely consistent with the presence of an extended linear π-conjugate system in which N(1) and N(3) exhibit strong negative and positive character, respectively, and in which N(2) displays small but significant positive character.

Experimental Section

1-Phenyl-3,3-pentamethylenetriazenes. The appropriate aromatic amine is diazotized at 0 °C. The resulting aryldiazonium ion mixture is treated with 1.1 equiv of piperidine. The mixture is extracted with ether, filtered, dried, and concentrated to yield the triazene. Triazene purity is at least 95% as determined by ^1H and ^{13}C NMR analysis. Yields are 30–95%.

Nuclear magnetic resonance spectra were obtained at 9.04 MHz on a Fourier transform multinuclear FX-90Q instrument without proton decoupling. Solutions of the triazene (40% by weight) in $CDCl_3$ contained in 10-mm sample tubes were measured at 30 °C. Approximately 30 mg of chromium(III) acetate was added to each sample to allow fast pulse repetition times (2 s, 45° pulse). Each sample required 17 000–25 000 scans to obtain spectra of approximately 5:1 signal-to-noise level (8000 Hz spectral width, 32K bits computer). Chemical shifts are reported relative to external $NH_4{}^{15}NO_3$ (17% in 10% HNO_3, 5% H_2O, 85% D_2O), which was measured separately and stored on disc. The instrument computer was set to zero on the standard before each chemical shift was recorded. Chemical shifts obtained in this manner are accurate to ±0.1 ppm.

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Registry No. 1 ($R = CH_3O$), 74148-29-1; 1 ($R = CH_3CH_2O$), 87261-58-3; 1 ($R = CH_3$), 51274-57-8; 1 ($R = H$), 16978-76-0; 1 ($R = F$), 332-01-4; 1 ($R = Cl$), 62499-15-4; 1 ($R = Br$), 87261-59-4; 1 ($R = CH_3CO$), 87261-60-7; 1 ($R = CN$), 87261-61-8; 1 ($R = NO_2$), 52010-83-0.

Enhanced Reducing Properties of Pyridine–Borane Adsorbed on Solid Supports: A Convenient Method for Chemoselective Reduction of Aldehydes

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Among the numerous reagents available for effecting the reduction of a carbonyl moiety to the corresponding alcohol is pyridine–borane. However, the latter is seldom utilized for this transformation since it reduces aldehydes and ketones only at elevated temperature.[1] Recently, one of us, while developing a methodology for the conversion of acid chlorides to the corresponding aldehydes,[2] observed that application of an equimolar mixture of an aldehyde and pyridine–borane to a column of Florisil led instantaneously[3] to a highly exothermic reaction, from which the alcohol corresponding to the aldehyde could be isolated in high yield. Since we have subsequently demonstrated that pyridine–borane remains structurally intact after being adsorbed on Florisil,[4] such results might be rationalized by citing the enhanced reducing properties amine–borane complexes are known[5] to exhibit in the presence of Lewis acids.

In view of the considerable attention focused in recent years on the use of solid supports to modify the reactivity of various reagents,[6] we decided to assess further the enhanced reducing capabilities of pyridine–borane adsorbed on solid supports. Initial experiments were performed by using silica gel to modify the reactivity of the borane complex since until recently[7] not many *reductions* had been examined in the presence of this support. Treatment[8] of a solution of benzaldehyde in cyclohexane with $^1/_3$ molar equiv of pyridine–borane in the presence of silica gel[9] re-

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[1] Barnes, R. P.; Graham, J. H.; Taylor, M. D. *J. Org. Chem.* **1958**, *23*, 1561.

[2] Babler, J. H. *Synth. Commun.* **1982**, *12*, 839.

[3] In contrast to these observations, IR analysis of an equimolar mixture of pyridine–borane and *p*-tolualdehyde indicated that no reaction between the neat components had occurred after 2 h at room temperature.

[4] Pyridine–borane, after being adsorbed for 15 min on solid supports such as Florisil, alumina, or silica gel can be recovered in quantitative yield by elution with ether.

[5] Andrews, G. C.; Crawford, T. C. *Tetrahedron Lett.* **1980**, *21*, 693 and references therein.

[6] For a review on organic syntheses using supported reagents, see: McKillop, A.; Young, D. W. *Synthesis* **1979**, 401–422, 481–500.

[7] Lithium aluminum hydride $LiAlH_4$-silica gel has been found to be more selective than $LiAlH_4$ itself and can reduce keto esters to the corresponding hydroxy esters. See: Kamitori, Y.; Hojo, M.; Masuda, R.; Inoue, T.; Izumi, T. *Tetrahedron Lett.* **1982**, *23*, 4585. Silica gel also appears to modify the reduction capability of sodium borohydride. See: Ciurdaru, V.; Hodosan, F. *Rev. Roum. Chim.* **1977**, *22*, 1027.

[8] The standard reduction procedure outlined in the Experimental Section was used for this reaction.

[9] Similar results were obtained with Florisil.