Letters to the Editor

^{1}H NMR Peak Assignment of 1-Aryl-3-methoxy-3-methyltriazenes

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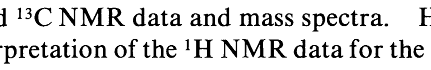
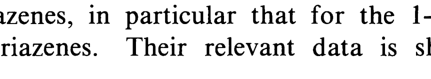
Giumanini and his colleagues [A. G. Giumanini, L. Lassiani, C. Nisi, A. Petric, and B. Stanovnik, *Bull. Chem. Soc. Jpn.,* **56**, 1887 (1983)] have discussed the structure of various aryldialkyltriazene *N*-oxides based on ^{1}H and ^{13}C NMR data and mass spectra. However, their interpretation of the ^{1}H NMR data for the 1-aryl-3-methoxy-3-methyltriazenes is inconsistent with that for other triazenes, in particular that for the 1-aryl-3,3-dimethyltriazenes. Their relevant data is shown in Table 1.

Table 1. ^{1}H NMR Data for 1-Aryl-3-methoxy-3-methyltriazenes and 1-Aryl-3,3-dimethyltriazenes



I



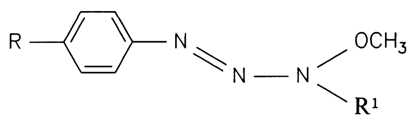
II

R	Chemical shift/ppm		
	I		II
	N-CH_3	O-CH_3	N(CH_3)$_2$
Cl	3.84	3.30	3.25
NO_2	3.88	3.65	3.28
			3.50

From this it can be seen that the chemical shifts assigned to the *O*-methyl group of compounds of type **I** are much more consistent with the chemical shifts of the *N*-methyl groups of compounds of type **II**, than are their *N*-methyl signals. In addition, variation in the aryl group substituents would be expected to have a far greater effect on the chemical shift of the *N*-methyl group than on that of the *O*-methyl. The assignments shown in Table 1 are at odds with this. It therefore seems likely that the ^{1}H NMR signals for the methyl groups of the 1-aryl-3-methoxy-3-methyltriazenes have been incorrectly assigned.

In order to confirm the correct assignment of the ^{1}H NMR signals suitably deuterated compounds have been synthesised, namely 1-(4-chlorophenyl)-3-methoxy-3-trideuteromethyltriazene (**2**) and 3-methoxy-1-(4-nitrophenyl)-3-trideuteromethyltriazene (**4**), by standard coupling procedures between the appropriate aryldiazonium salt and *O*-methyl-*N*-trideuteromethylhydroxylamine [D. E. V. Wilman, P. J. Cox, P. M. Goddard, L. I. Hart, K. Merai, and D. R. Newell, *J. Med. Chem.,* **27**, 870 (1983)]. The *O*-methyl-*N*-trideuteromethylhydroxylamine was prepared from *O*-methylhydroxylamine after the method of Goel and Krolls using hexadeuterodimethylsulphate (MSD Isotopes) in place of dimethylsulphate [O. P. Goel and U. Krolls, *Org. Prep. Proced. Int.,* **19**, 75 (1987)]. Melting points and NMR spectra were in line with those previously reported. Nuclear magnetic resonance spectra were obtained on a Bruker AC250 spectrometer, for solutions in deuterochloroform maintained at 297 K with tetramethylsilane as internal standard.

Table 2. ^{1}H NMR of 1-Aryl-3-methoxy-3-methyltriazenes



III

	R	R^1	Chemical shift/ppm	
			N-CH_3	O-CH_3
1	Cl	CH_3	3.37	3.88
2	Cl	CD_3		3.88
3	NO_2	CH_3	3.50	3.93
4	NO_2	CD_3		3.92

The ^{1}H chemical shifts of the *N*- and *O*-methyl groups of the various 1-aryl-3-methoxy-3-methyltriazenes are displayed in Table 2. These results show that the ^{1}H chemical shift of the *N*-methyl group of the 1-aryl-3-methoxy-3-methyltriazenes is in the region of δ=3.3 to 3.5 and the *O*-methyl group is situated at approximately δ=3.9. These results are at variance with the peak allocation made by Giumanini and his colleagues.