Inorganica Chimica Acta, 47 (1980) 77–79
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Sulphur-Nitrogen Compounds.
VII*. Electron Spin Resonance and Nitrogen-15 Nuclear Magnetic Resonance Observations on the Formation and Structure of Tris(arylsulphonyl)hydroxyl amines

ROBERT A. DAVIE and CHRISTOPHER GLIDEWELL**
Chemistry Department, University of St. Andrews, St. Andrews, Fife KY16 9ST, U.K.

Received June 3, 1980

Samples of $(ArSO_2)_3NO$ prepared by non-oxidative methods do not exhibit ESR spectra in solution: the observation of $(ArSO_2)_2NO^{\cdot}$ ESR spectra in samples of $(ArSO_2)_3NO$ prepared oxidatively shows therefore that the $(ArSO_2)_2NO^{\cdot}$ are guenine residual intermediates from the oxidation of $(ArSO_2)_2NOH$. ^{15}N chemical shifts of arylsulphonamides and arylsulphonylhydroxylamines show that the product of oxidation of $(ArSO_2)_2NOH$ is an N,N,O trisubstituted hydroxylamine $(ArSO_2)_2NOSO_2Ar$, rather than an N,N,N trisubstituted amine oxide $(ArSO_2)_3\overset{+}{N}-\overset{-}{O}$.

Introduction

The oxidation of N,N-bis(arylsulphonyl)hydroxylamines, $(ArSO_2)_2NOH$ (Ar = 4-XC_6H_4; X = H, F, Cl, CH_3, CH_3O), yields [2] products of composition $(ArSO_2)_3NO$ by a route thought to involve successive formation of the radicals $(ArSO_2)_2NO^{\cdot}$ and $ArSO_2^{\cdot}$. Apparently analytically pure samples of $(ArSO_2)_3NO$, for X = H, F, Cl, CH_3, but not CH_3O, give [3] in benzene solution ESR signals characteristic of the aminyl oxides $(ArSO_2)_2NO^{\cdot}$, even though the same solutions give sharp well resolved NMR spectra. The aminyl oxide radicals could arise either as an intermediate in the oxidative conversion of $(ArSO_2)_2NOH$ to $(ArSO_2)_3NO$, or by spontaneous homolysis of $(ArSO_2)_3NO$ in solution.

The NMR spectra of $(ArSO_2)_3NO$ indicate the presence of two types of ring (^1H, X = CH_3O; ^{19}F, X = F; ^{13}C, X = F, Cl, CH_3CH_3O) but the spectra of $(ArSO_2)_2NOH$ indicate only a single ring environment.

The present paper represents ESR evidence which effectively rules out the possibility of spontaneous homolysis of $(ArSO_2)_3NO$, and a ^{15}N NMR study of $(ArSO_2)_nNH_{3-n}$, $ArSO_2NHOH$, $(ArSO_2)_2NOH$ and $(ArSO_2)_3NOH$ for X = CH_3, which unambiguously shows that the product of oxidation of $(ArSO_2)_2$-NOH is $(ARSO_2)_2NOSO_2Ar$ rather than the amine oxide $(ArSO_2)_3\overset{+}{N}-\overset{-}{O}$.

Experimental

Literature methods were used for the preparation of $(CH_3C_6H_4SO_2)_2NH$ [4], $(CH_3C_6H_4SO_2)_3N$ [5], $CH_3C_6H_4SO_2NHOH$ $(CH_3C_6H_4SO_2)_2NOH$ [2], $(C_6H_5SO_2)_3NO$ [2], $(CH_3C_6H_4SO_2)_3NO$ [2] and $(CH_3SO_2)_2NH$ [6]. ^{15}N NMR spectra were recorded at P.C.M.U., Harwell, using a Bruker WH-180 FT spectrometer operating at 18.24 MHz: the chemical shifts recorded in Table I are for solutions approximately 0.2 *M* in DMSO, and are referred to external $CH_3^{15}NO_2$. Chemical shift differences on change of solvent, *e.g.* to acetone were usually no more than ±1 ppm; broad-band ungated proton decoupling was employed throughout. ESR spectra were recorded using a Decca X-3 spectrometer.

Results and Discussion

ESR Spectra

The compounds $(ArSO_2)_3NO$ can be prepared not only by oxidation of $(ArSO_2)_2NOH$, but also [2] by reaction of $(ArSO_2)_2NOH$ with $ArSO_2Cl$ in the presence of base, equation (1):

$$(ArSO_2)_2NOH + ArSO_2Cl + B \rightarrow B{\cdot}HCl + (ArSO_2)_3NO \qquad (1)$$

Samples prepared by this route, for X = H, CH_3 gave no detectable ESR spectra, even at the detection limits of the spectrometer, under conditions identical with those in which samples prepared by oxidation gave extremely strong spectra. We therefore conclude that no spontaneous homolysis of

---

*Part VI, Ref. 1.

**Author to whom all correspondence should be addressed.

TABLE I. ^{15}N Chemical Shifts (ppm) for Tolylsulphonamides and Tolylsulphonylhydroxylamines.

$CH_3C_6H_4SO_2NH_2$	−284.5	$CH_3C_6H_4SO_2NHOH$	−226.1
$(CH_3C_6H_4SO_2)_2NH$	−220.9	$(CH_3C_6H_4SO_2)_2NOH$	−170.9
$(CH_3C_6H_4SO_2)_3N$	−159.8	$(CH_3C_6H_4SO_2)_3NO$	−143.0

TABLE II. Other Sulphonamide ^{15}N Chemical Shifts (ppm).

H_3NSO_3	−286.4^a	$C_6H_5SO_2NH_2$	−285.9^b
$H_2NSO_3^-$	−287.1^a	$CH_3SO_2NH_2$	−286.0
$NH(SO_3)_2^{-2}$	−225.8^a	$(CH_3SO_2)_2NH$	−222.8
$N(SO_3)_3^{-3}$	−153.3^a		

^{a}Ref. 7. ^{b}Ref. 8.

$(ArSO_2)_3NO$ occurs in solution to yield $(ArSO_2)_2NO^•$, but that when radicals $(ArSO_2)_2NO^•$ are present in samples of $(ArSO_2)_3NO$ [3], they are residual intermediates from the oxidation process. This direct observation of a genuine intermediate is strong evidence for the correctness of the reaction scheme put forward earlier [2, 3].

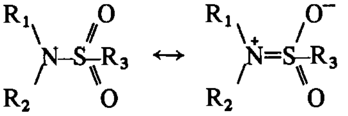
^{15}N *NMR Spectra*

Chemical shifts of tolylsulphonylamides and tolylsulphonylhydroxylamines are recorded in Table I, and a number of other relevant shifts for related compounds are given in Table II.

The chemical shift of ammonia is −380.2 ppm [9] and successive introduction of sulphonyl groups, whether neutral or anionic, aliphatic or aromatic, induces paramagnetic shifts of *ca.* 100 ppm, 60 ppm, and 60 ppm: the contrast between this behaviour and that of successive carbon substitution at nitrogen has been noted previously [7].

The chemical shift of unprotonated hydroxylamine, NH_2OH appears to be unknown. Values recorded for the corresponding cation, NH_3OH^+, are −276 ppm (^{14}N shift) [10], and −293 ppm [11]: the difference between these values arises from differences in concentration, solvent, or referencing. In general protonation of aliphatic amines causes a downfield shift of *ca.* 10 ppm [12], so that a value of −275 ppm will probably not be greatly in error for the shift in NH_2OH: as with NH_3, successive introduction of two sulphonyl groups causes paramagnetic shifts, each of *ca* 50 ppm, and it is necessary to consider the difference in the chemical shifts expected, on the one hand for an N,N,O-tris(arylsulphonyl)hydroxylamine, $(ArSO_2)_2NOSO_2Ar$ and on the other hand for an N,N,N-tris(arylsulphonyl)amine oxide $(ArSO_2)_3NO$.

Oxidation of $(ArSO_2)_3N$ to the amine oxide $(ArSO_2)_3NO$ is expected, *via* the local paramagnetic term to lead to a marked shielding of ^{15}N nucleus, and a consequent marked upfield chemical shift. The strong deshielding of the nitrogen nucleus on introduction of sulphonyl groups may be a consequence [13] both of the presence of many low lying excited states, (resulting from the presence of sulphur 3d orbitals) and of multiple bonding involving the nitrogen lone pair, thus:



$ArSO_2$ is certainly a deactivating group in electrophilic aromatic substitution [14], and evidence for such N–S π-interactions can be derived from the structures of a number of ions and molecules. N–S π-interactions will be maximised when the nitrogen atom is planar: planar nitrogen is found in, for example $HN(SO_3)_2^{-2}$ [15], $ON(SO_3)_2^{-2}$ [16], $N(SO_3)_3^{-3}$ [17], $(CH_3SO_2)_2NH$ [18] and $(PhSO_2)_2NH$ [19]: Glemser has suggested [20] a bond length-bond order correlation for sulphur–nitrogen bonds which yields bond orders as follows, based on experimentally determined bond distances: $HN(SO_3)_2^{-2}$ [15], 1.08; $ON(SO_3)_2^{-2}$ [16], 1.08; $N(SO_3)_3^{-3}$ [17], 0.90; $(CH_3SO_2)_2NH$ [18], 1.14; $(PhSO_2)_2NH$ [19], 1.12; $PhSO_2NC_9H_{16}O$ [21], 1.18; $CH_3C_6H_4SO_2NHCH_2Ph$ [22], 1.25; and $(PhSO_2)_2N^-$ [19], 1.42. These data fully support the occurrence of multiple N–S bonding in sulphonamide species, and indicate that when the lone pair of electron on nitrogen is removed by quaternisation, *e.g.* on oxidation, a substantial upfield shift is expected. Some examples of such shifts in various classes of compound are given in Table III: even taking the minimum value of those recorded this would give a chemical shift for the amine oxide $(ArSO_2)_3NO$ at least as negative

TABLE III. ^{15}N Shifts (ppm) on Oxidation of Nitrogen Atoms.

Molecule, X	$\Delta\delta$[a]
NO_2^-	−232
PhNO	−541
BuONO	−235
PhCN	−49
C_5H_5N	−25
PhNNPh	−172
PhCHNPh	−40

[a] $\Delta\delta = \delta N (XO) - \delta N (X)$ resulting from the oxidation of X to XO: source, ref. 13.

as −185 ppm; the shift is possibly substantially more negative.

The alternative formulation $(ArSO_2)_2NOSO_2Ar$ results from a substitution of H by SO_2Ar in $(ArSO_2)_2NOH$: since by analogy with $(PhSO_2)_2NH$ [19] and $ON(SO_3)_2^{-2}$ [16], the nitrogen atom in $(ArSO_2)_2NOH$ is expected [2] to be planar, no significant change occurs on substitution at oxygen other than replacement of the electroneutral hydrogen atom by the strongly electron withdrawing $ArSO_2$ group. Hence the principal effect on the ^{15}N chemical shift of this substitution is *via* the local diamagnetic term, and in this example, a marked *downfield* shift is expected, from the value of −171 ppm observed in $(ArSO_2)_2NOH$.

Since the expected values of δ(N) for $(ArSO_2)_3NO$ and $(ArSO_2)_2NOSO_2Ar$ respectively fall on either side of the value in $(ArSO_2)_2NOH$, a structural distinction can readily be made on the basis of the observed shift, −143 ppm, which shows clearly that the correct constitution is $(ArSO_2)_2NOSO_2Ar$. This deduction, based on direct NMR observation of the crucial atom, nitrogen, is in accord with deductions made from observations of nuclei (^1H, ^{13}C, ^{19}F) only indirectly influenced by the configuration at nitrogen.

Acknowledgement

We thank S.R.C. for an allocation of ^{15}N spectrometer time at P.C.M.U., Harwell.

References

1 Part VI; A. R. Butler and C. Glidewell, *J. Chem. Research,* (S)239, (M)3201 (1978).
2 J. D. Birchall and C. Glidewell, *J. Chem. Soc. Dalton,* 10 (1977).
3 J. D. Birchall and C. Glidewell, *J. Chem. Soc. Dalton,* 604 (1978).
4 N. N. Dykhanov, *Zhur. Obsh. Khim., 29,* 3602 (1959).
5 H. Stetter and H. Hansmann, *Chem. Ber., 90,* 2728 (1957).
6 B. Helferich and H. Flechsig, *Chem. Ber., 75,* 532 (1942).
7 N. Naulet, G. J. Martin, J.-J. Barieux, and J.-F. Combroux, *J. Chem. Research,* (S)158 (1980).
8 I. I. Schuster, S. H. Doss, and J. D. Roberts, *J. Org. Chem., 43,* 4693 (1978).
9 P. R. Srinivasan and R. L. Lichter, *J. Magn. Resonance, 28,* 227 (1977).
10 D. Herbison-Evans and R. E. Richards, *Mol. Phys., 8,* 19 (1964).
11 M. Witanowski and H. Januszewski, *Can. J. Chem., 47,* 1321 (1969).
12 R. O. Duthaler and J. D. Roberts, *J. Am. Chem. Soc., 100,* 3889 (1978).
13 G. C. Levy and R. L. Lichter, 'Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy', Wiley-Interscience, New York (1979).
14 H. H. Jaffe, *Chem. Rev., 53,* 191 (1953).
15 D. W. J. Cruickshank and D. W. Jones, *Acta Cryst., 16,* 887 (1963).
16 R. A. Howie, L. S. D. Glasser, and W. Moser, *J. Chem. Soc. A,* 3043 (1968).
17 J. V. Tillak and C. H. L. Kennard, *J. Chem. Soc. A,* 1637 (1970).
18 R. Attig and D. Mootz, *Acta Cryst., B31,* 1212 (1975).
19 F. A. Cotton and P. F. Stokely, *J. Am. Chem. Soc., 92,* 294 (1970).
20 O. Glemser, A. Müller, D. Böhler and B. Krebs, *Z. Anorg. Chem., 357,* 184 (1968).
21 S. Sato, T. Yoshioka and C. Tamura, *Acta Cryst., B31,* 1385 (1975).
22 T. S. Cameron, K. Prout, B. Denton, R. Spagna and E. White, *J. Chem. Soc. Perkin II,* 176 (1975).