

# E.s.r. Studies of the Generation and Structure of Aminosulphonyl (Sulphamoyl) Radicals, R<sub>2</sub>NSO<sub>2</sub>·

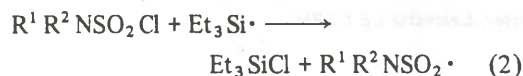
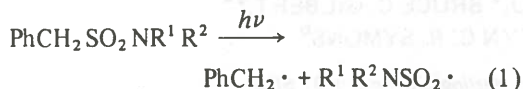
*J. Chem. Research (S)*,  
1980, 185  
*J. Chem. Research (M)*,  
1980, 2610-2623

CHRYSSOSTOMOS CHATGILIALOGLU,<sup>a</sup> BRUCE C. GILBERT,<sup>a\*</sup>  
RICHARD O. C. NORMAN,<sup>a</sup> and MARTYN C. R. SYMONS<sup>b</sup>

<sup>a</sup>Department of Chemistry, University of York, Heslington, York YO1 5DD

<sup>b</sup>Department of Chemistry, University of Leicester, Leicester LE1 7RH

The isotropic and anisotropic e.s.r. spectra of a series of aminosulphonyl radicals, R<sup>1</sup>R<sup>2</sup>NSO<sub>2</sub>·, have been measured. These radicals can be detected (together with the benzyl radical in some instances) when solutions of phenylmethanesulphonamides in diethyl ether are irradiated at *ca.* 170 K [reaction (1)] or when Et<sub>3</sub>Si· reacts with aminosulphonyl chlorides [reaction (2)] under similar conditions. The isotropic spectra (see Table) are characterized by splittings of similar magnitude (*ca.* 0.5 mT) from <sup>14</sup>N and both α (N-H) and β (N-CH<sub>3</sub>) protons.

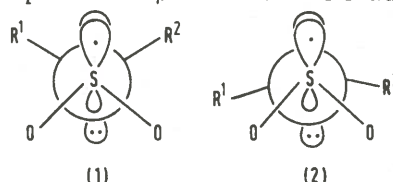


Radiolysis of solid samples of aminosulphonyl chlorides, either as pure compounds or as solid solutions in either 2-methyltetrahydrofuran or tetramethylsilane also leads to the appropriate aminosulphonyl radicals, the results for <sup>14</sup>N and <sup>1</sup>H being in good agreement with those obtained from the photolysis of fluid solutions; little anisotropy in these splittings is discerned. In addition, satellites from <sup>33</sup>S are observed (see Table). Other radicals detected include amino-radicals ·NR<sup>1</sup>R<sup>2</sup> (e.g. R<sup>1</sup>, R<sup>2</sup> = H, Me), which suggests that reaction (3) is accompanied by reaction (4)



(a signal attributed to an intermediate radical-anion is observed for piperidine-1-sulphonyl chloride), as well as radicals which may be derived *via* electron-loss (e.g.

·NHSO<sub>2</sub>Cl, from ·H<sub>2</sub>NSO<sub>2</sub>Cl, and several species thought to be σ\*-dimers [R<sub>2</sub>NSO<sub>2</sub>Cl-ClSO<sub>2</sub>NR<sub>2</sub>·]). Analysis of the <sup>33</sup>S-splittings indicates that the radicals are essentially sulphur-centred, with over 50% of the unpaired electron on sulphur and pyramidal character at this atom (*p/s* ratio *ca.* 4.7). Accordingly they are best formulated as R<sub>2</sub>NSO<sub>2</sub>· (rather than, say, ·NR<sub>2</sub>SO<sub>2</sub>·), with a structure in-between that of the analogous species<sup>16</sup> ·SO<sub>3</sub>· and that of alkane-sulphonyl radicals<sup>15</sup> RSO<sub>2</sub>·. The *g* values (*ca.* 2.0035) are considerably less than those of the π-type radicals<sup>4</sup> R<sub>2</sub>NS· and R<sub>2</sub>NS=O (*cf.* also RSO<sub>2</sub>· with RS· and RSO·). Finally, the magnitude and similarity of the α- and β(CH<sub>3</sub>)-proton splittings suggest that these arise *via* a small amount of spin density in a *p*(π)-type orbital on nitrogen in structures of type (1) or (2); in these, it is argued, the through-bond spin-polarization transmission of spin density to the protons is relatively ineffective. These structures contrast with those for ·CONH<sub>2</sub> and ·CONHMe, in which the orbital of the unpaired electron is believed to be in the same plane as the β N-H and N-C bonds.<sup>19</sup>



Technique used: E.s.r. spectroscopy      References: 29  
Table 2: Characteristics of the orbital containing the unpaired electron in aminosulphonyl and related radicals calculated from <sup>33</sup>S splittings

References cited in this synopsis:

- <sup>4</sup>J. A. Baban and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1978, 678.  
<sup>15</sup>M. Geoffroy and E. A. C. Lucken, *J. Chem. Phys.*, 1971, 55, 2719.  
<sup>16</sup>P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.  
<sup>19</sup>H. Hefter and H. Fischer, *Ber. Bunsenges. Phys. Chem.*, 1970, 74, 493.

Table 1 E.s.r. data for aminosulphonyl radicals, R<sup>1</sup>R<sup>2</sup>NSO<sub>2</sub>·

R <sup>1</sup>	R <sup>2</sup>	Method of generation <sup>a</sup>	Isotropic hyperfine splittings <sup>b</sup>			A <sub>  </sub> ( <sup>33</sup> S) <sup>c</sup>	A <sub>⊥</sub> ( <sup>33</sup> S) <sup>c</sup>	g <sub>iso</sub> <sup>d</sup>
			a(N)	a(H)	a(CH <sub>3</sub> )			
H	H	A, B	0.500	0.500		11.8	8.0	2.0036
		C	0.5	0.5				2.0035
H	Me	A, B	0.580	0.580	0.450	12.0	8.4	2.0036
		C	0.55	0.55	0.55			2.0035
Me	Me	B	0.690		0.522	11.8	7.6	2.0036
		C	0.70		0.70			2.0035
<sup>2</sup> H	<sup>2</sup> H	A	0.500		0.077(2 <sup>2</sup> H)			2.0036
	[CH <sub>2</sub> ] <sub>s</sub>	C				12.0	7.8	2.0035

<sup>a</sup>A, Photolysis of PhCH<sub>2</sub>SO<sub>2</sub>NR<sup>1</sup>R<sup>2</sup> in diethyl ether at *ca.* 170 K.

B, Photolysis of R<sup>1</sup>R<sup>2</sup>NSO<sub>2</sub>Cl/Bu<sup>t</sup>OObu<sup>t</sup>/Et<sub>3</sub>SiH solutions in toluene or in diethyl ether at *ca.* 170 K.

C, Radiolysis of solid samples (as pure compounds as well as solutions in 2-methyltetrahydrofuran and in tetramethylsilane).

<sup>b</sup>± 0.01 mT for solution spectra; ± *ca.* 0.1 mT for solid-state spectra.

<sup>c</sup>± 0.3 mT.

<sup>d</sup>± 0.0001 for solution spectra, ± 0.0005 for solid-state spectra.