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An ESR Study of *N*-Sulfonylaminyls[1)]

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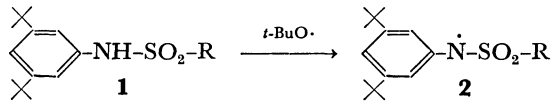
Synopsis. *N*-(3,5-Di-*t*-butylphenyl)-*N*-sulfonylaminyls, 3,5-*t*-$Bu_2C_6H_3$-$\dot{N}$-SO_2-R, were investigated by means of ESR spectroscopy. The a_N values are 7.8 G, and the a_H values due to the *N*-phenyl ring protons are 5.6 (*o*-H) and 7.6 G (*p*-H). However, no couplings due to the protons in R have been detected. From these results, it is concluded that the unpaired electron is located on the nitrogen atom and the *N*-phenyl ring, negligibly delocalized onto the sulfonyl group.

N-Sulfonylaminyls have been of considerable interest as intermediates in chemical and photochemical reactions.[2)] However, the radicals have little been investigated by means of ESR spectroscopy.[3)] Recently, we have examined some nitrogen-centered free radicals in which one or two divalent sulfur atoms are adjacent to the central nitrogen.[1)] Sulfonylaminyls are also of interest in comparison with the nitrogen-centered free radicals from the point of view of ESR spectroscopy. In this paper we will report an ESR study of *N*-(3,5-di-*t*-butylphenyl)-*N*-sulfonylaminyls (**2**).

The radicals **2** were generated in benzene by hydrogen-abstraction from sulfonamides, **1**, by *t*-butoxyl which



was obtained on the pyrolysis of di-*t*-butyl diperoxyoxalate.[4)] The ESR parameters for **2** are listed in Table 1, and a typical ESR spectrum is illustrated in Fig. 1. As can be seen from the figure, well-resolved spectra were recorded in any case by this procedure. However, some peaks in the signals were gradually broadened with the passage of time (*ca.* 1 h). This may be caused by the occurrence of a secondary radical which could not be identified.

The ESR parameters for **2** are quite different from those reported for sulfonyl nitroxides, $RN(O\cdot)SO_2R'$, ruling out the possibility that **2** are nitroxides.[5)]

The a_H values of **2** are considerably large and are constant within the limits of experimental error, regardless of the sulfonyl groups. On the other hand, no couplings due to the sulfonyl protons have ever been detected. From these results, it is obvious that the unpaired electron is located on the nitrogen and the *N*-phenylring, negligibly delocalized onto the sulfonyl group. The *g*-values for **2** are 2.0033, which is approximately equal to that for a typical nitrogen-centered free radical, diphenylaminyls (2.0032)[6)] or 3,4-dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl (2.0033).[7)] In contrast, the *g*-value (2.0059) of the *N*-(arylthio)aminyl, **3**, is considerably larger than those of **2**.[8)]

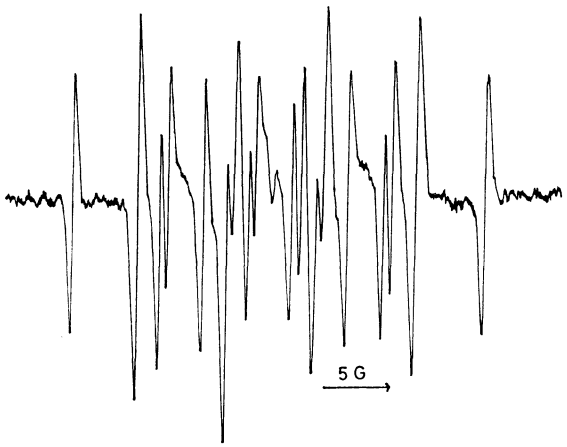


Fig. 1. An ESR spectrum of **2a** in benzene at room temperature.

The results obtained for **2** are consistent with those for the sulfonyl-conjugated radicals, $\cdot CR_1R_2SO_2R_3$,[9)] in which the unpaired electron is not delocalized onto the sulfonyl group. In the case of **3**,[8)] on the other hand, the unpaired electron is delocalized to some extent onto the *S*-phenyl ring.

On the basis of the results and discussion, it is concluded that sulfonyl groups have not ability to delocalize the unpaired electron in *N*-sulfonylaminyls, much as in the case of the sulfonyl-conjugated carbon radicals.[9)]

Experimental

All the melting points are uncorrected. The IR spectra were run on a JASCO IR-G Spectrometer, while the NMR

Table 1. The ESR parameters for *N*-(3,5-di-*t*-butylphenyl)-*N*-sulfonylaminyls (**2**)[a)]

	Radical[b)]	a_N[c)]	$a_{o\text{-}H}$[c,d)]	$a_{p\text{-}H}$[c,d)]	*g*-Value
2a	R-$\dot{N}$-SO_2-C_6H_5	7.75	5.63	7.56	2.0033
2b	R-$\dot{N}$-SO_2-$C_6H_4CH_3$-*p*	7.79	5.64	7.62	2.0033
2c	R-$\dot{N}$-SO_2-CH_3	7.79	5.59	7.57	2.0033
3[e)]	R-$\dot{N}$-S-C_6H_4Cl-*p*	9.58	3.70	4.42	2.0059

a) In benzene at room temperature. b) R: 3,5-Di-*t*-butylphenyl. c) In gauss. d) Due to the *N*-phenyl ring protons. e) The a_H value due to the *S*-phenyl ortho-protons: 0.75 G; see Ref. 8.

spectra were recorded with a Hitachi-Perkin Elmer R-20 Spectrometer, using TMS as the internal standard. 3,5-Di-*t*-butylaniline[10] and di-*t*-butyl diperoxyoxalate[4] were prepared by the reported methods.

Preparation of Sulfonamides. A solution of sulfonyl chloride (0.010 mol), 3,5-di-*t*-butylaniline (0.0097 mol), and triethylamine (0.011 mol) in dry ether (200 ml) was stirred for two days at room temperature. After the reaction mixture was filtered, ether was removed by evaporation and the resulting residue was subjected to column-chromatography [Mallinckrodt, silica gel (100 mesh), eluent: benzene/hexane: 15/1], followed by recrystallization from appropriate solvents.

N-*(3,5-Di-*t*-butylphenyl)benzenesulfonamide (**Ia**).* Colorless prisms with a mp of 144—145 °C (from benzene/hexane: 1/5, then hexane). Yield: 80%. IR (KBr): 3200 (NH) and 1170 cm^{-1} (SO_2). NMR ($CDCl_3$): δ 1.20 (s, *t*-Bu, 18H) and 6.82—7.85(m, C_6H_3 and C_6H_5, 8H). Found: C, 69.94; H, 7.51; N, 3.98%. Calcd for $C_{20}H_{27}NO_2S$: C, 69.52; H, 7.88; N, 4.05%.

N-*(3,5-Di-*t*-butylphenyl)-*p*-toluenesulfonamide (**Ib**).* Colorless prisms with a mp of 173—175 °C (from benzene/hexane: 1/10, then hexane). Yield: 82%. IR (KBr): 3200 (NH) and 1150 cm^{-1} (SO_2). NMR ($CDCl_3$): δ 1.20 (s, *t*-Bu, 18H), 2.35 (s, CH_3, 3H), and 6.85—7.76 (m, C_6H_3 and C_6H_4, 7H). Found: C, 70.22; H, 8.20; N, 3.90%. Calcd for $C_{21}H_{29}NO_2S$: C, 70.15; H, 8.13; N, 3.90%.

N-*(3,5-Di-*t*-butylphenyl)methanesulfonamide (**Ic**).* Colorless needles with a mp of 134—136 °C (from hexane). Yield 56%. IR (KBr): 3300 and 3200 (NH) and 1160 and 1140 cm^{-1} (SO_2). NMR ($CDCl_3$): δ 1.30 (s, *t*-Bu, 18H), 2.98 (s, CH_3, 3H), 6.95 (bs, NH, 1H), and 7.05—7.27 (m, C_6H_3, 3H). Found: C, 63.87; H, 8.67; N, 5.00%. Calcd for $C_{15}H_{25}NO_2S$: C, 63.56; H, 8.89; N, 4.94%.

ESR Spectra. Sulfonamide (20 mg), di-*t*-butyl peroxyoxalate (30 mg), and benzene (0.4 ml) were placed in an ESR tube, after which the solution was degassed by three freeze-and-thaw cycles, then sealed. The ESR signals were recorded at room temperature (*ca.* 21 °C) on a JES-ME-3X Spectrometer with an X-band microwave unit and 100 KHz field modulation.

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