Push-Pull Nitrogen Free Radicals from Benzenesulphonanilides or Benzanilides with Donor *para*-Substituents

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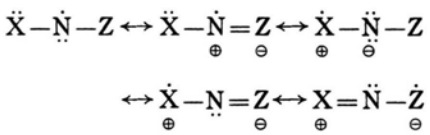
(Z. Naturforsch. 28b, 543–544 [1973]; received April 5, 1973)

ESR spectra, phenylogy

It was pointed out[1] that nitrogen free radicals have enhanced stability if they are sterically shielded and possess push-pull electronic effects. Combination of electron-donor groups $\ddot{X}$ (such as alkoxy, dialkyl- or diarylamino) with acceptor groups Z (such as arenesulphonyl, aroyl, 2,4,6-tri-, 2,4-di- or 2,6-dinitrophenyl, 2,4,6-tricyano- or -tricarbomethoxyphenyl) yields nitrogen free radicals **1** which do not react with oxygen and can be observed in solution by ESR spectroscopy in stationary systems; in some cases they can even be isolated in crystalline state. In addition to nitrogen free radicals with structures resulted from the above combinations, their *p*-phenylogues **2** are also stable. Thus *p*-phenylogues of diphenylpicrylhydrazyl[2] or of picrylalkoxyaminyl[3] were prepared. Recently, the preparation and ESR spectra of 1,1-diphenyl-2-arenesulphonylhydrazyls (**3**) were reported,[4] whereas 1,1-diphenyl-2-aroylhydrazyls (**4**) have been known for a longer time[5]. In the present paper we report the preparation and ESR spectra of *p*-phenylogues **5** and **6** of free radicals **3** and **4**, respectively.



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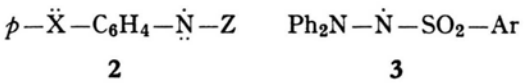
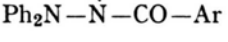


2 **3**



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5

6

Arenesulphonanilides were prepared from arenesulphonyl chlorides and substituted anilines in pyridine. Their oxidation with lead tetraacetate in benzene, dioxane or dichloromethane afforded coloured solutions of **5** (Ar = C_6H_5, *p*-$C_6H_4CH_3$, *p*-$C_6H_4NO_2$, X = Me_2N, Ph_2N, MeO) giving well-resolved ESR spectra in stationary systems at room or lower temperatures. Thus **5** (X = Me_2N), irrespective of the Ar group, presents an ESR spectrum with 31 lines at –40 °C (Figure); at room temperature the half-life is about one min. excepting the *p*-nitrobenzenesulphonyl derivative which is stable for a longer time. The *g*-value is 2.0031 ± 0.0001. This value rules out a nitroxidic structure which would require a *g*-factor of approx. 2.006. Coupling constants determined with a computer program[6] are : 6.2 G (one aminyl nitrogen), 6.2 G (two *o*-hydrogens), 4.2 G (one *p*-amino nitrogen), 4.2 G (six methyl hydrogens), 2.1 G (two *m*-hydrogens).

Figure. First-derivative ESR spectrum of **5**, Ar = *p*-$C_6H_5NO_2$, X = NMe_2, in methylene dichloride at –40 °C.

Radicals **5** (X = Ph_2N, irrespective of the Ar group) are even more stable. At –40 °C they present an ESR spectrum with a large number of lines which make the interpretation difficult; at –20 °C to +30 °C, however, six lines are obtained (*g*-factor 2.0032), with coupling constants 8.8 G (one hydrogen), 4.4 G (one hydrogen) and 4.4 G (one nitrogen), passing gradually during approx. 10 min. into a five-line ESR spectrum (*g*-factor 2.0034) with coupling constant 4.9 G (two nitrogen nuclei). These complex transformations may involve[7] loss of SO_2 from the radical **5** and are under study.

Similar oxidation of benzanilide (**6**) (Ar = Ph, X = Ph_2N) in dichlorometane at –30 °C affords a five-line ESR spectrum with coupling constant 6.2 G due to two nitrogen nuclei and *g*-factor 2.0031.

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