Radical Anions of Trimethylsilyl-substituted *NN*-Dimethylanilines

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The introduction of a trimethylsilyl ring substituent sufficiently enhances the electron affinity of *NN*-dimethylanilines to permit metal reduction to radical anions in mixed ether solvents. The e.s.r. spectra of the radical anions of *o*-, *m*-, and *p*-trimethylsilyl-*NN*-dimethylaniline, the first examples of *NN*-dialkylaniline radical anions which do not have strongly electron-withdrawing ring substituents, are reported. They indicate that the electron-withdrawing effect of the trimethylsilyl group in the ground states of radical anions is equal to or slightly greater than the strong electron-donating effect of the dimethylamino-group.

THE cation radicals of substituted anilines may be readily prepared by oxidation of the parent aniline. The e.s.r. spectra of several such cation radicals have been reported.[1,2] However, the same electron-releasing effect of the amino-substituent which facilitates oxidation, decreases the electron affinity of the molecule, and hinders reduction to radical anions. When this electron donation is counteracted by a strong electron-withdrawing group in the ring, reduction can be achieved. Thus, nitroanilines may be reduced and the e.s.r. spectra of several such radical anions have been reported.[3]

Gerson and his co-workers have shown that the reduction of anilines may also be achieved when the electron-donating effect of nitrogen is diminished through trimethylsilyl substitution at nitrogen.[4] In both *NN*-bis(trimethylsilyl)aniline and *NNN'N'*-tetrakis(trimethylsilyl)-*p*-phenylenediamine radical anion the unpaired electron is found in a predominantly antisymmetric π^* orbital, as is evidenced by the equal or nearly equal splittings for the *ortho*- and *meta*-protons, and a very small coupling due to the *para*-proton in *NN*-bis(trimethylsilyl)aniline. To our knowledge, there are no other reports of aniline radical anion e.s.r. spectra.

Recently Sipe and West found that, in radical anions of trimethylsilyl- or trimethylgermyl-alkylbenzenes, the organometallic substituent completely dominated the spin distribution by accepting electron density more efficiently than the alkyl groups release it.[5] This result is consistent with the minor perturbations of aromatic radical anions produced by alkyl substituents, which, in many cases, barely lift the degeneracy of the benzene symmetric and antisymmetric π^* orbitals;[6] and the much larger effects observed for silyl-substituted aromatic radical anions.[7] The effect of silicon substitution on aromatic radical anions which also bear a strongly perturbing substituent such as the dimethylamino-group has not hitherto been investigated.

RESULTS AND DISCUSSION

We report the first examples of aniline radical anions which do not have strongly electron-withdrawing ring substituents such as the nitro-group. In our previous studies we demonstrated that the trimethylsilyl group is

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[1] M. J. Drews, P. S. Wong, and P. R. Jones, *J. Amer. Chem. Soc.*, 1972, **94**, 9122.

[2] B. M. Latta and R. W. Taft, *J. Amer. Chem. Soc.*, 1967, **89**, 5172.

[3] D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Amer. Chem. Soc.*, 1962, **86**, 987.

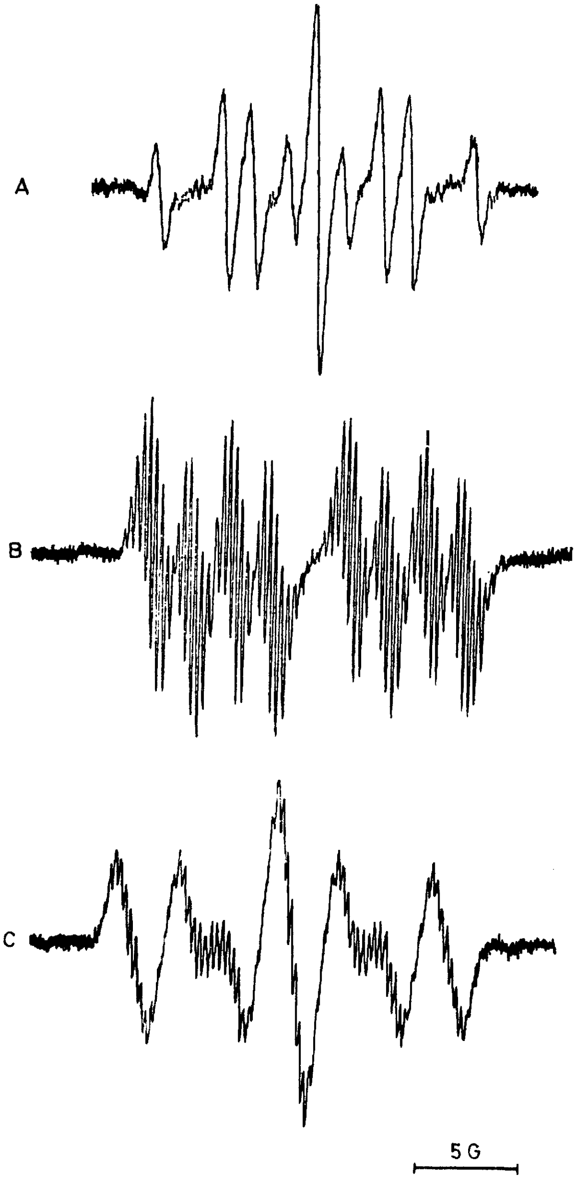
[4] F. Gerson, U. Krynitz, and H. Bock, *Angew. Chem. Internat. Edn.*, 1969, **8**, 767.

[5] H. J. Sipe and R. West, *J. Organometallic Chem.*, 1974, **70**, 353, 367.

[6] E. De Boer and J. P. Colpa, *J. Phys. Chem.*, 1967, **71**, 21; P. R. Jones, D. E. Wood, and I. N. Jung, unpublished results.

[7] Y. P. Wan, D. H. O'Brien, and F. J. Smentowski, *J. Amer. Chem. Soc.*, 1972, **94**, 7680 and references therein.

slightly electron withdrawing in the ground states of *para*-substituted *NN*-dimethylanilines.[1,8] The electronic spectra of these molecules led us to expect an even more pronounced electron withdrawal in the excited states.[9] We therefore attempted the alkali metal reduction of alkyl- and trimethylsilyl-substituted *NN*-dimethylanilines. While all our attempts to generate ring alkylated aniline radical anions were unsuccessful, we have found that the substitution of a trimethylsilyl group in any ring position increases the electron affinity of *NN*-dimethylanilines to the point where metal reduction to the radical anions is feasible despite the effects of the strongly electron-releasing dimethylamino-group. The e.s.r. spectra of these anions are shown in the Figure.



E.s.r. spectra for the radical anions of A, *p*-trimethylsilyl-*NN*-dimethylaniline; B, *o*-trimethylsilyl-*NN*-dimethylaniline; C, *m*-trimethylsilyl-*NN*-dimethylaniline: 2 : 1 tetrahydrofuran–dimethoxyethane, −90°, potassium as the reducing agent

The spectrum of *p*-trimethylsilyl-*NN*-dimethylaniline radical anion, A, consists of two triplets, 4·55 and 3·25 G, due to two sets of equivalent ring protons. An expanded spectrum permits the measurement of a smaller splitting of 0·15 G arising from the trimethylsilyl protons. No coupling of the unpaired electron with the protons or nitrogen of the dimethylamino-group, or with potassium was resolved. The *o*-trimethylsilyl-*NN*-dimethylaniline radical anion spectrum, B, is assigned as four doublet splittings of 8·48, 3·60, 1·72, and 0·50 G from four non-equivalent ring protons and a splitting of 0·26 G due to the trimethylsilyl protons. For *m*-trimethylsilyl-*NN*-dimethylaniline radical anion the spectrum, C, consists of four doublets of 7·35, 4·25, 2·67, and 0·78 G due to the ring protons and a splitting by the trimethylsilyl protons of 0·23 G. As with the *para*-compound, neither the *ortho*- nor *meta*-substituted radicals showed resolvable splittings which could be attributed to the dimethylamino-group or to potassium. Careful hydrolysis and reisolation of a sample which gave the spectrum of *p*-trimethylsilyl-*NN*-dimethylaniline anion showed that no cleavage of the dimethylamino-group from the radical had occurred. Each of the spectra shown in the Figure was reproduced by computer simulation using the coupling constants given.

For both *o*- and *m*-trimethylsilyl-*NN*-dimethylaniline radical anions the largest ring proton coupling constants and those for the trimethylsilyl protons are comparable to the splittings observed for the *para*-proton (8·18 G) and the trimethylsilyl protons (0·26 G) in trimethylsilylbenzene radical anion,[5] for which it is clear that the unpaired electron resides in the π^* orbital symmetrical to the mirror plane defined by silicon.[10] Labelling experiments for both *o*- and *m*-trimethylsilyl-*NN*-dimethylaniline show that the largest spin density in the radical anions occurs at the ring position *para* to the trimethylsilyl group.[11] Thus, for both these anilines, the interaction of the highest occupied orbital in the radical anion with the trimethylsilyl substituent is more important than the electron-donating effect of the dimethylamino-group.

The splittings observed for *p*-trimethylsilyl-*NN*-dimethylaniline are intermediate between those anticipated for a ‘ pure ’ symmetric or antisymmetric π^* orbital; *viz.*, 5·1 and 5·7 G for *NN*-bis(trimethylsilyl)aniline,[4] or 1·06 and 2·66 G for trimethylsilylbenzene.[5] If one assumes a McConnell type relation between the observed coupling constants, a_i, and the π spin densities, ρ_{Ci}:[12]

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[8] P. R. Jones, M. J. Drews, J. K. Johnson, and P. S. Wong, *J. Amer. Chem. Soc.*, 1972, **94**, 4595.

[9] M. J. Drews and P. R. Jones, *J. Organometallic Chem.*, 1974, **82**, 57.

[10] J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, 1963, **59**, 53.

[11] I. N. Jung and P. R. Jones, unpublished results.

[12] H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 764; H. M. McConnell and D. B. Chestnut, *ibid.*, 1958, **28**, 107.

$a_i = \rho_{Ci}Q$ and a value for Q of 23 G;[13] the spin densities at the *ortho*- and *meta*-carbons of *p*-trimethylsilyl-*NN*-dimethylaniline may be calculated as 0·14 and 0·20 respectively. These values account for 68% of the total spin density and leave 32%, or nearly 1/3 of the total spin density, to be distributed between the *para*-carbons and the substituents. On this basis the spin distribution for the *para*-substituted compound is similar to that for benzene radical anion itself. It appears that the electron-withdrawing effect of the trimethylsilyl group and the electron-releasing effect of the dimethylamino-group nearly cancel each other. It should be noted that this type of spin distribution has been predicted for cases in which the donor and acceptor strengths of substituents are nearly equal in disubstituted aromatic radical anions.[5] If the donor strength of the dimethylamino-group and the acceptor strength of the trimethylsilyl group were equal, however, then we would expect 'benzene type' spin distributions for the *ortho*- and *meta*-compounds. This is contrary to what is observed. We are led to the conclusion that the ability of the trimethylsilyl group to accept electron density is more important than the ability of the dimethylamino-group to release it in aniline radical anions. Nevertheless, the trimethylsilyl group does not completely dominate the spin distribution as was the case for the alkyl substituted organometal aromatic radical anions.

The diminished importance of the dimethylamino-group's effect on spin distribution in these compounds may be a phenomenon associated with aniline radical anions in general, and not a direct result of trimethylsilyl substitution on the ring. The coupling constants for the dimethylamino-groups in all three of the aniline radical anions reported here must be <0·2 G. In contrast, the protons and nitrogen of the amino-group in *p*-nitro-*NN*-dimethylaniline radical anion give splittings of 0·71 and 1·13 G respectively.[3] For *o*-trimethylsilyl-*NN*-dimethylaniline the small nitrogen coupling constant may be attributed to steric inhibition of interaction. However, for the *meta*- and *para*-compounds, where steric effects should be negligible, and in several other aniline radical anions which we are currently investigating, the coupling with the dimethylamino-group is still too small to be resolved.[11] It thus appears that nitroanilines represent unusual cases and that in typical aniline radical anions the nitrogen coupling will be found to be small. It is conceivable that, in systems where the additional electron occupies a predominantly aromatic orbital, electron repulsion between the additional electron and the nitrogen lone pair results in a twisting of the dimethylamino-group out of conjugation. This would result in a decrease in both the electron donating ability and the hyperfine coupling of the amino-group. We have obtained some preliminary evidence for this effect in CNDO calculations for silyl-substituted aniline radical anions. In the minimum energy geometry for these anions the nitrogen approaches tetrahedral hybridization and is twisted so as to decrease interaction between the lone pair and the aromatic π system. Geometry considerations for aniline radical anions will be the subject of a future publication.

EXPERIMENTAL

The aniline radical anions were obtained by reduction with potassium in mixed ether solvents at low temperatures. In a typical experiment, the aniline, purified by preparative g.l.c. immediately prior to use, was dissolved to give a *ca.* 10^{-4}M solution in 2 : 1 tetrahydrofuran–dimethoxyethane which had been purified in the usual manner.[14] Potassium metal which had been rinsed with pentane was triply sublimed *in vacuo* to finally produce a metal mirror coating on a high surface area Vigereaux type tube. The aniline solution was brought into contact with the mirror and held at −196° for 1 h while the typical blue colour developed. The radical was then developed at −78°. Spectra were recorded with sample temperatures between −90 and −70°. Above −70° the radicals' signals rapidly decayed.

The e.s.r. spectra were recorded on a Varian V-4502-13 spectrometer with 100 kHz field modulation using the Varian low temperature probe. Coupling constants were measured from expanded scale spectra and not from the spectra obtained for publication.

In one case, a sample which gave the spectrum of *p*-trimethylsilyl-*NN*-dimethylaniline radical anion was carefully opened and hydrolysed with anhydrous ethanol. Analysis of the mixture by g.l.c. showed only tetrahydrofuran, dimethoxyethane, ethanol, and *p*-trimethylsilyl-*NN*-dimethylaniline to be present. No trimethylsilylbenzene, an anticipated product if cleavage of the dimethylamino group had occurred, was observed.

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[13] J. R. Bolton in 'Radical Ions,' eds. E. T. Kaiser and L. Kevan, Interscience, New York, 1968, pp. 9—12.

[14] P. R. Jones and R. West, *J. Amer. Chem. Soc.*, 1968, **90**, 6978.