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SUBSTITUENT EFFECTS OF TRIALKYLSILYL AND TRIALKYLGERMYL GROUPS: THE ELECTRON SPIN RESONANCE SPECTRA OF NITROBENZENE RADICAL ANIONS

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SUMMARY

The ESR spectra of the radical anions of *o*-, *m*-, and *p*-(trimethylsilyl)- and *p*-(triethylgermyl)nitrobenzene have been measured in methanol solutions. The ^{14}N isotropic hyperfine interactions are discussed in terms of the substituent effects of the organometallic groups. Satellite spectra from ^{29}Si and ^{73}Ge have also been observed.

INTRODUCTION

Because of their stability and ease of preparation substituted nitrobenzene radical anions have been extensively studied by electron spin resonance. The radicals have been prepared by chemical reduction with, for example, alkali metals[1], sodium dithionite[2] and glucose[3], by electrolytic reduction in both aqueous[4] and non-aqueous solvents[5,6] and photochemically[3,7]. These investigations have led to a number of interesting correlations with other physical and chemical properties. The most obvious effects are found in the ESR spectra of *p*-substituted nitrobenzene radical anions. For a considerable number of such compounds, the nitrogen coupling constant has been shown to be sensitive to the nature of the substituent. Relative to nitrobenzene the splitting increases for electron repelling groups and decreases for electron withdrawing ones. The order of substituent effects thus found correlates well with, for example, polarographic half wave potentials, Hammett σ constants[5], and the partial rate factors for *p*-nitration of the parent compound[8]. As the nitrogen coupling constants are solvent dependent it is important to use data from a single solvent system when making comparisons.

The substituent effect of MR_3 groups, where M is a group IV B element, is a subject of some current interest and we have investigated the ESR spectra of the *o*-, *m*-, and *p*-(trimethylsilyl)- and *p*-(triethylgermyl)nitrobenzene radical anions. The ^{14}N NMR spectra of the silicon compounds have recently been reported[9] and it is possible to compare results from the two methods and with data on other radicals containing trimethylsilyl groups[10-14]. The ESR spectra of the *m*- and *p*-(trimethylsilyl)nitrobenzene radicals have recently been measured in acetonitrile and DMF solutions under somewhat lower resolution than in the present work[15].

RESULTS AND DISCUSSION

All of the compounds studied were easily reduced using any of the methods previously mentioned. However, alkali metal reduction can give rise to ion pairing which complicates the spectrum[15]. There is some advantage in working with hydroxylic solvents since the larger nitrogen splitting gives spectra with fewer overlapping lines. The most straightforward technique which gave satisfactory spectra was steady state photolysis of the nitro compound in methanol solutions containing sodium methoxide[3]. The irradiations were carried out in the cavity of a Varian E3 spectrometer with a 250 watt mercury lamp focused by a quartz lens. The solutions were purged with nitrogen prior to photolysis to reduce line broadening.

TABLE 1

HYPERFINE COUPLING CONSTANTS OF SUBSTITUTED NITROBENZENE RADICAL ANIONS (GAUSS)

Position	$PhNO_2$	o-$Me_3SiC_6H_4NO_2$	m-$Me_3SiC_6H_4NO_2$	p-$Me_3SiC_6H_4NO_2$	p-$Et_3GeC_6H_4NO_2$
a_N	13.60	13.04	13.66	13.16	13.47
a_H^o	3.52	3.48	3.45	3.35	3.40
a_H^m	1.14	1.12	1.12	1.08	1.11
a_H^p	3.71	3.48	3.60		
a_{Si}				2.76	
a_{Ge}					1.25

The analysis of the spectra is straightforward; the coupling constants are given in Table 1 and some of the spectra are shown in Fig. 1. We were unable to resolve any structure from the protons in the alkyl groups but from the line widths we estimate any such splitting is less than 0.05 G.

We have also investigated the wings of each spectrum under increased gain with the hope of seeing coupling from the 4.7% of ^{29}Si and 7.6% of ^{73}Ge present in natural abundance. Satellite peaks were found in the wings of each spectrum. Most of these were attributable to ^{13}C but by comparison with nitrobenzene it was possible to extract a ^{29}Si coupling of 2.76 ± 0.25 G for the p-radical. ^{73}Ge has a spin of 9/2 and gave an easily recognised progression of satellite peaks with a splitting of 1.25 G. It has been estimated[16] that a single unpaired electron in a silicon 3s orbital would have a coupling constant of 1208 G; the corresponding figure for the 4s orbital of germanium is 535 G. Using these values the observed splittings both correspond to an unpaired electron density of 0.23% on the heteroatom.

Molecular orbital calculations

To assist in the interpretation of the results we have performed calculations on each of the radicals using McLachlan's approximate SCF method[17] with $\lambda = 1.2$. The parameters for nitrogen and oxygen were taken from previous work on fluoronitrobenzenes[18] ($\alpha_N = \alpha + 2.2\ \beta$, $\alpha_O = \alpha + 1.88\ \beta$, $\beta_{CN} = 1.20\ \beta$, $\beta_{NO} = 1.67\ \beta$). For silicon and germanium we have used the parameters of Curtis and Allred[11,12] ($\alpha_{Si} = \alpha - 1.2\ \beta$, $\beta_{SiC} = 0.45\ \beta$, $\alpha_{Ge} = \alpha - 1.05\ \beta$, $\beta_{GeC} = 0.30\ \beta$). The latter values were chosen on the basis of Huckel calculations and are not necessarily optimised for the McLachlan procedure. However, because of the substantial negative spin densities found in the

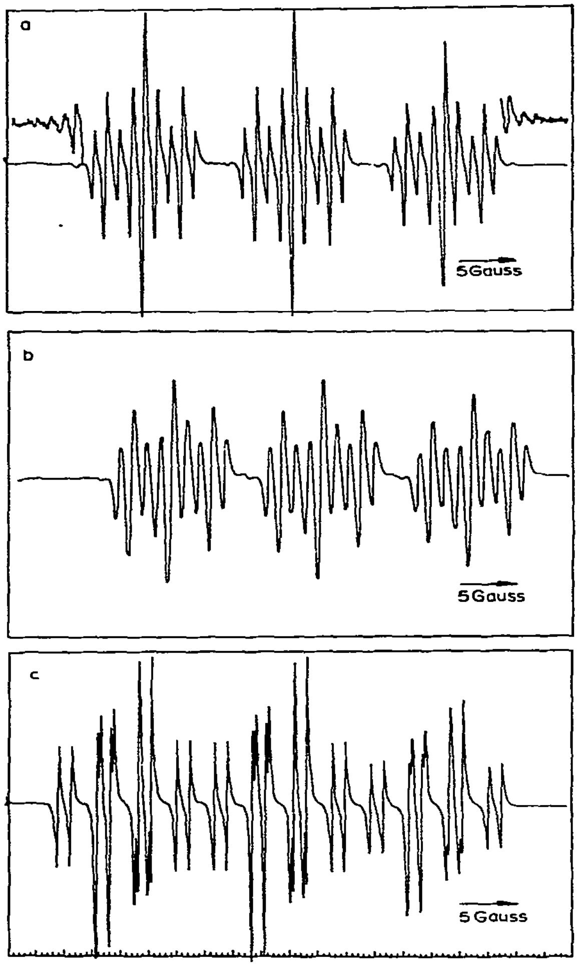

Fig. 1. The ESR spectra in methanol solutions of the radical ions of (a) *p*-(trimethylsilyl)nitrobenzene (the wings are shown under increased gain to illustrate the ^{29}Si and ^{13}C satellites), (b) *o*-(trimethylsilyl)nitrobenzene and (c) *m*-(trimethylsilyl)nitrobenzene.

m-position of nitrobenzene radical anions, the Huckel approximation is not very useful in the present instance. The results are given in Table 2 together with experimental spin densities determined from the proton hyperfine splittings and McConnell's relationship. The calculations give a reasonable account of the trends in coupling constants found for the various substituents, in particular the magnitude of the ^{14}N splitting correlates with the spin densities on nitrogen and oxygen.

The parameters of Allred and coworkers[11,12] seem to work well with the present compounds and there is little point in attempting to optimise them further.

The influence of the trialkylmetal substituents on the nitrogen coupling constants is qualitatively in agreement with the electronic effect of these groups on rates and equilibria observed in other systems[19]. Electron release by the trimethylsilyl substituent from the *m*-position would explain the increase in coupling constant

TABLE 2

COMPARISON OF EXPERIMENTAL AND THEORETICAL SPIN DENSITIES

Position	$PhNO_2$		o-$Me_3SiC_6H_4NO_2$		m-$Me_3SiC_6H_4NO_2$		p-$Me_3SiC_6H_4NO_2$		p-$Et_3GeC_6H_4NO_2$	
	Theor.	Exptl.[a]	Theor.	Exptl.	Theor.	Exptl.	Theor.	Exptl.	Theor.	Exptl.
0	0.1827		0.1799		0.1820		0.1777		0.1797	
N	0.3219		0.3085		0.3207		0.3049		0.3122	
1	−0.0371		−0.0274		−0.0370		−0.0273		−0.0320	
2	0.1508	0.1564	0.1518		0.1465	0.1533	0.1428	0.1489	0.1464	0.1511
3	−0.0538	−0.0510	−0.0540	−0.0498	−0.0518		−0.0468	−0.0480	−0.0503	−0.0493
4	0.1559	0.1649	0.1484	0.1546	0.1602	0.1601	0.1523		0.1540	
5	−0.0538	−0.0510	−0.0642	−0.0498	−0.0543	−0.0498	−0.0468	−0.0480	−0.0503	−0.0493
6	0.1508	0.1564	0.1365	0.1546	0.1552	0.1533	0.1428	0.1489	0.1464	0.1511
7[b]			0.0225		−0.0034		0.0228		0.0143	

[a] The experimental spin densities have been obtained by dividing the proton hyperfine coupling constants by 22.5; their signs are undetermined but have been chosen to agree with the theoretical values. [b] Metal π-orbital.

relative to nitrobenzene although the observed difference lies within the experimental errors and may not be significant. From the *p*-position, an electron-withdrawing resonance effect outweighs inductive electron release to the carbon framework atom of the aromatic ring with consequent reduction in the coupling constant. As expected, the effect is greater for silicon than for germanium.

Distortions arising from steric contributions cannot be ruled out in assessing the effect of the *o*-trimethylsilyl substituent. Any out-of-plane deformation of the nitro group would lead to increased spin density on nitrogen and hence an increase in the coupling constant. However, through-space interactions could well account for the observed lowering of this value.

The nitrogen coupling constant in the *p*-tert-butylnitrobenzene radical anion in aqueous methanol has been reported[3] as 14.0 G. Taken in conjunction with our results this value confirms the conclusions of Bedford *et al.*[10] that *p*-trialkylsilyl and -germyl groups are electron attracting relative to hydrogen whereas tert-butyl is electron repelling. The ^{14}N chemical shifts of the nitrophenyl trimethylsilanes show $\delta_p > \delta_m > \delta_o$ and have been taken as evidence for conjugation in the *p*-compound. Inductive effects are largest in the *o*-compound which is also sensitive to steric interactions[9].

Studies of trimethylsilyl-substituted aromatic hydrocarbons have shown that ^{29}Si coupling constants are of the same order of magnitude as the values for protons attached to a carbon atom with the same π-electron spin density[13]. We can write $a(^{29}\mathrm{Si}) = Q \cdot \rho_\mathrm{C}$ where $|Q| = 17.8$ G. There does not appear to be any comparable data on ^{73}Ge coupling constants in the literature. From our results we estimate a $|Q|$ for these splittings of 7.8 G.

EXPERIMENTAL

o-, *m*-, and *p*-(Nitrophenyl)trimethylsilanes were prepared by nitrodesilylation of the respective *o*-, *m*-, and *p*-bis(trimethylsilyl)benzenes[20]. *p*-(Nitrophenyl)triethylgermane[21] was similarly prepared from *p*-bis(triethylgermyl)benzene. Purity of products was established by analytic gas–liquid chromatography (5′ SE 60 column at 200°).

ESR measurements were made on methanol solutions containing the appropriate nitro compound (*ca.* 10^{-3} *M*) and sodium methoxide (*ca.* 10^{-2} *M*). The sweep of the Varian E3 spectrometer was calibrated with aqueous solutions of Fremy's salt ($a_\mathrm{N} = 13.09$ G) and coupling constants were measured to within ±1%.

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