Radical Anions and Nitroxides from Alkylthio-, Alkylsulphinyl-, and Alkylsulphonyl-nitrobenzenes

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The e.s.r. spectra of the radical anions and nitroxides from nitrobenzenes substituted with SR, SOR, and SO_2R groups are reported. The effect of the substituent on the spin density distribution as revealed by the variations of the nitrogen and ring protons splitting constants, is discussed. While the alkylsulphinyl and alkylsulphonyl groups behave as electron attractors, their electron-withdrawing ability being little dependent on the nature of the alkyl substituent, the alkylthio-group has an electron-acceptor character strongly dependent on the dimensions and therefore on the conformation of the aliphatic substituent. As a possible explanation it is suggested that σ-π conjugation with electron release from the π orbital containing the unpaired electron to the low lying σ^* antibonding orbital of the C–S bond is responsible for this behaviour.

SULPHUR containing radicals have been extensively investigated during recent years;[1,2] however attention has been mainly focused on heterocyclic compounds such as thiophen and related derivatives. Sulphides, sulphoxides, and sulphones show little tendency to give radical anions and only very few have been investigated by e.s.r. spectroscopy.[2] Stabilization of these derivatives in their reduced form can however be achieved by association with extensively conjugated π-systems, or with strongly electronegative substituents such as the nitro-group.

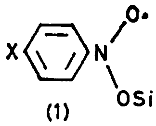
We report here an e.s.r. study of the radical anions from nitrobenzenes substituted at the *ortho*-, *meta*-, and *para*-positions with alkylthio, alkylsulphinyl, and alkylsulphonyl groups. The nitroxides obtained by photolysing some of the nitrobenzenes in triethylsilane have also been investigated. The effect of the substituent on the spin density distribution is discussed.

Nickel(II)-induced proton contact shifts have also been measured in the substituted anilines corresponding to the *para*-nitro-derivatives examined.

EXPERIMENTAL

Substituted nitrobenzenes and anilines were prepared as reported in the literature. The nitrobenzenes were reduced to radical anions by treatment with potassium t-butoxide in dimethyl sulphoxide (DMSO) solution.

The radical anions of the *p*-methylthio-, -ethylthio-, and -t-butylthio-derivatives were also generated by photolysis in methanol containing sodium methoxide and the e.s.r. spectra were recorded at low temperature to try to freeze out the rotational motion of the substituent. Since no spectral changes were observed above −60 °C, the energy barrier to the rotation of these groups should have an upper limit of $<$*ca.* 5—6 kcal mol^{-1}. Nitroxides were generated in the cavity of the e.s.r. spectrometer, by irradiation of deoxygenated solutions of the nitrobenzenes in triethylsilane with a 100 W mercury lamp. This method leads to nitroxides of general formula (1), as the result of the addition to the nitro-



(1)

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[1] L. Lunazzi, A. Mangini, G. F. Pedulli, and M. Tiecco, *Gazzetta*, 1971, **101**, 10.

[2] M. M. Urberg and E. T. Kaiser, in 'Radical Ions,' eds. E. T. Kaiser and L. Kevan, Interscience, New York, 1968.

benzenes of triethylsilyl radicals produced by hydrogen abstraction from triethylsilane by nitroarene triplets.[3] In no case could nitroxides be obtained from *ortho*-substituted nitrobenzenes.

Although in monoaryl nitroxides the rotation of the nitroxide function is known to be relatively slow even at room temperature, the non-equivalence of the two *ortho*-protons is too small to be resolved in the e.s.r. spectrum as has been previously observed in the unsubstituted phenyl triethylsilyloxy nitroxide.[3]

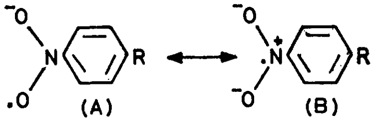
The hyperfine splitting constants reported in Tables 1—5 were measured at room temperature.

The proton resonance shifts of the substituted anilines were measured at room temperature relative to internal tetramethylsilane to eliminate bulk susceptibility. The contact shifts were determined in [^{2}H]chloroform (*ca.* 1M) by adding increasing amounts of $Ni(acac)_2$ to the aniline solution. The chemical shifts were plotted against the $Ni(acac)_2$ concentration and from the slopes relative shifts were obtained.

RESULTS AND DISCUSSION

The hyperfine splitting constants of the radical anions and nitroxides of the substituted benzenes examined are reported in Tables 1—5. The assignment of the coupling constants to the various positions is straightforward in the *para*-derivatives, while there is some doubt concerning the attribution to 2- and 6-H in the *meta*-substituted nitrobenzenes and to the 3- and 5-H in the *ortho*-derivatives.

The nitrogen splitting constant in substituted nitroanions may be taken as a measure of the electron-releasing or -withdrawing power of the ring substituent. In fact electron-repelling groups as *para*-alkyl or -alkoxy induce an increase in a_N by increasing the relative importance of the mesomeric structure (B) with respect to (A). On the other hand electron-withdrawing substituents such as cyano, carbonyl, or nitro are well known to decrease substantially the nitrogen splitting constant.



From the data of Tables 1—5 replacement of one phenyl proton with SCH_3, $SOCH_3$, or SO_2CH_3 induces a decrease in the nitrogen splitting whatever the substituted position. The decrease in a_N is larger the greater is the oxidation state of sulphur. The smaller reduction of a_N observed for the *ortho*- with respect to the *para*-derivatives should be due to the steric interaction with the nitro-group or the nitroxide function which prevents conjugation from being so effective.

To quantify the effect of *para*-substitution, the σ constants of the three groups were determined by referring to the Hammett equation derived by Bowers for a series of substituted nitrobenzenes,[4] since classical σ values generally do not correlate well with e.s.r. data. The calculated σ values are 0.040, 0.260, and 0.464 for SCH_3, $SOCH_3$, and SO_2CH_3 respectively. This means that even the methylthio-group behaves as an electron-withdrawing substituent with a strength similar to that of chlorine and bromine.

TABLE 1

Hyperfine splitting constants (G) of the radical anions of *para*-substituted nitrobenzenes measured in DMSO and, in parentheses, in 1 : 1 CH_3OH–dimethoxyethane containing sodium methoxide

Substituent	a_N	$a_{2,6}$	$a_{3,5}$	a_R	
OMe	11.05	3.36	1.08	0.31	
	(14.12)	(3.34)	(1.06)	(0.33)	
OEt	11.06	3.35	1.07	0.30	(2 H)
	(14.16)	(3.36)	(1.06)	(0.38)	
Me	10.36	3.37	1.06	4.02	
	(13.59)	(3.33)	(1.12)	(3.68)	
H	9.89	3.32	1.04	3.94	
	(13.23)	(3.33)	(1.12)	(3.58)	
SMe	9.53	3.38	1.12	0.23	
	(12.86)	(3.32)	(1.15)	(0.34)	
SEt	9.30	3.34	1.08		
	(12.77)	(3.35)	(1.18)		
SBu^t	8.78	3.28	0.99		
	(12.27)	(3.32)	(1.13)		
SOMe	8.14	3.25	0.91	0.32	
SOEt	8.17	3.18	0.89		
$SOBu^t$	8.00	3.15	0.89		
SO_2Me	7.03	3.11	0.70	0.84	
SO_2Et	6.99	3.11	0.69	0.69	(2 H)
SO_2Pr^i	6.96	3.10	0.61	0.61	(1 H)
SO_2Bu^t	6.84	3.01	0.58		

TABLE 2

Hyperfine splitting constants (G) for the *para*-substituted phenyl triethylsilyloxy nitroxides $RC_6H_4N\dot{O}OSiEt_3$ in triethylsilane solution

Substituent	a_N	$a_{2,6}$	$a_{3,5}$	a_R	
OMe	15.82	3.06	0.96	0.36	
OEt	15.76	3.04	0.96	0.36	(2 H)
Me	15.12	3.06	1.03	3.34	
H	14.86	3.12	1.02	3.19	
SMe	14.63	3.15	1.12	0.38	
SEt	14.48	3.15	1.11	0.23	(2 H)
SBu^t	14.03	3.12	1.08		
SOMe	13.91	3.10	1.05		
SOEt	13.87	3.12	1.08		
SO_2Me	13.23	3.13	1.02	0.52	
SO_2Et	13.09	3.09	1.03	0.46	(2 H)
SO_2Pr^i	13.09	3.09	1.03	0.26	(1 H)
SO_2Bu^t	13.10	3.06	1.02		

TABLE 3

Hyperfine splitting constants (G) of the radical anions of *meta*-substituted nitrobenzenes measured in DMSO and, in parentheses, in 1 : 1 CH_3OH–dimethoxyethane containing sodium methoxide

Substituent	a_N	a_2	a_4	a_5	a_6	a_R
OMe	10.00	3.29	3.78	1.00	3.29	
	(12.86)	(3.31)	(3.50)	(1.07)	(3.13)	
Me	9.97	3.37	3.86	1.04	3.37	1.04
	(13.37)	(3.34)	(3.57)	(1.07)	(3.34)	(1.07)
SMe	9.53	3.31	3.94	1.00	3.31	
	(12.83)	(3.33)	(3.54)	(1.07)	(3.33)	
SBu^t	9.61	3.34	4.18	1.02	3.34	
	(12.93)	(3.34)	(3.65)	(1.12)	(3.34)	
SOMe	8.86	3.26	4.23	1.00	3.26	
$SOBu^t$	9.04	3.22	4.14	1.01	3.40	
SO_2Me	8.45	3.08	4.32	0.98	3.49	0.14
SO_2Bu^t	8.58	3.13	4.39	1.02	3.56	

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[3] C. M. Camaggi, L. Lunazzi, G. F. Pedulli, G. Placucci, and M. Tiecco, *J.C.S. Perkin II*, 1974, 1226.

[4] K. W. Bowers, ref. 2, ch. 5.

Table 4

Hyperfine splitting constants (G) of the *meta*-substituted phenyl triethylsilyloxy nitroxides $RC_6H_4N\dot{O}OSiEt_3$ in triethylsilane solution

Substituent	a_N	a_2	a_4	a_5	a_6	a_R
OMe	14.73	3.02	3.02	0.98	3.02	
Me	14.86	3.07	3.13	1.01	3.07	1.01
SMe	14.66	3.15	3.15	1.02	3.15	
SBu^t	14.62	3.14	3.14	1.05	3.14	
SOMe	14.23	3.14	3.14	1.01	3.14	
$SOBu^t$	14.47	3.12	3.12	1.03	3.12	
SO_2Me	14.10	3.14	3.14	1.04	3.14	
SO_2Bu^t	14.11	3.13	3.13	1.01	3.13	

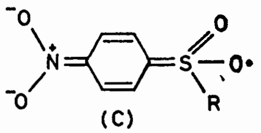
Table 5

Hyperfine splitting constants (G) of the radical anions of *ortho*-substituted nitrobenzenes measured in DMSO

Substituent	a_N	a_3	a_4	a_5	a_6	a_R
OMe	10.56	0.90	3.92	1.05	3.55	
SMe	9.69	0.97	4.01	1.20	3.51	0.44
SOMe	8.99	1.07	4.22	1.15	3.41	0.13
SO_2Me	7.53	0.64	4.12	1.29	2.83	0.64

A comparison of the a_N variations in the *ortho*-, *meta*-, and *para*-compounds shows that the effect of methylthio-substitution is practically the same in the three positions. This seems to indicate that the SCH_3 group influences the spin density distribution only through its inductive effect, and behaves always as a weakly electron-withdrawing group at variance with the methoxy-group which is an acceptor in *meta*- * and a donator in *ortho*- and *para*-derivatives.

In the methylsulphinyl and methylsulphonyl derivatives a_N is much smaller for the *ortho*- and *para*- than for the *meta*-derivative, thus indicating that these groups also exert a considerable conjugative effect with delocalisation of the unpaired electron in the substituent itself, as exemplified by structure (C) for the negative radical of *p*-alkylsulphonylnitrobenzene.



(C)

A most striking result has been observed by changing the alkyl group in the *p*-alkylthionitrobenzenes or nitroxides, as the variations of the nitrogen splittings are much greater than could be reasonably expected.[5] Furthermore, the large difference of the a_N values measured in the *para*- and *meta*-t-butylthio derivatives, leads to the exclusion of the possibility that the attracting character of the sulphur atom is due only to its inductive effect as instead it could be inferred from the data relative to the methylthio-substituted compounds. Actually the much smaller nitrogen splitting observed in the *para*-derivative implies that a large resonance contribution is responsible for the strong withdrawing power of the t-butylthio-group in that position.

Solvent effects, operating through steric inhibition of solvation in the larger alkylthio-compounds, may also be discarded since the a_N variations show the same trend in media of increasing solvating capability, *i.e.* triethylsilane, dimethyl sulphoxide, methanol, and water.

The most straightforward interpretation of this result involves participation to the π-system of the vacant $3d$ orbitals of the sulphur atom and then expansion of its valence shell. Since however the electron-acceptor character of the alkylthio-group is strongly dependent on the dimensions of the aliphatic substituent, we prefer the following explanation. The *p*-nitrothioanisole anion is likely to be planar or nearly planar because of the weak steric interaction between the methyl and *meta*-protons; in this conformation the resonance contribution of the alkylthio-group in modifying the nitrogen splitting constant should be very low, and the weak electron-acceptor character almost exclusively arises from its inductive effect. When increasing the size of the alkyl substituent the greater steric crowding should favour a conformation in which the SR group sits above the molecular plane so that the sulphur–carbon bond is essentially eclipsed by the $2p_z$ orbital on C-4. In the latter conformation overlap between the π-system on the nitrobenzene moiety and the S–C σ-bond is at a maximum and therefore σ-π conjugation might become an important interaction. Consequently we may expect electron release to or from the π-system depending on the relative energies of the π-orbital containing the unpaired electron and of the occupied and vacant orbitals of the carbon–sulphur bond. In the present case, the large decrease of the nitrogen splitting observed by substituting the *para*-proton with a t-butylthio-group, indicates that electron release takes place from the singly occupied π orbital to the σ^* antibonding orbital of the C–S link. This interpretation is supported by preliminary INDO calculations which will be fully reported elsewhere.[6]

Information on the conjugative properties of the substituents may also be obtained from the hyperfine splittings at the alkyl protons, provided their sign is known.

The most obvious way of determining the sign of hyperfine splitting constants in organic radicals is to measure their n.m.r. spectra. Because of the difficulties involved in using this technique, mainly concerning product solubility, we preferred to employ an alternative method, *i.e.* the complexation of anilines carrying the same substituents as our nitrobenzenes, with nickel(II) acetylacetonate. Nickel induced n.m.r. contact shifts provide both the relative magnitude and sign of the spin density at the coupled protons. Since the shifts measured in substituted anilines correspond reasonably

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* An exception to this trend is provided by the anion of *m*-nitroanisole in DMSO solution, in which the OCH_3 group behaves as a weakly donor substituent. Solvent effects may be responsible for this anomaly.

[5] J. R. Bolton, A. Carrington, A. Forman, and L. E. Orgel, *Mol. Phys.*, 1962, **5**, 43; E. de Boer and J. P. Colpa, *J. Phys. Chem.*, 1967, **71**, 21.

[6] A. Alberti, M. Guerra, C. Martelli, F. Bernardi, and G. F. Pedulli, to be published.

well to the e.s.r. splittings of the negative radicals of nitrobenzenes,[7] the result can be transferred with some confidence to our original systems. From Table **6**, which report n.m.r. contact shifts of anilines *para*-substituted by OCH_3, SCH_3, $SOCH_3$, and SO_2CH_3 groups, the coupling at the methyl protons increases parallel to the hyperfine splitting constants measured in the nitrobenzene anions, always being positive as previously found by Torssell and his co-workers [8] on similarly substituted aryl-t-butyl nitroxides. This means that α spin density is localized on sulphur (or oxygen in the *p*-methoxy-derivatives) and transmitted to the methyl protons *via* a hyperconjugative mechanism, giving rise to a positive splitting. The way spin density may be acquired by the sulphur or oxygen in the *p*-methylthio and *p*-methoxy nitroxides and, to a lesser extent, nitroanions, certainly involves some contribution to the mesomeric system by polar structures such as (E).[8]

TABLE 6

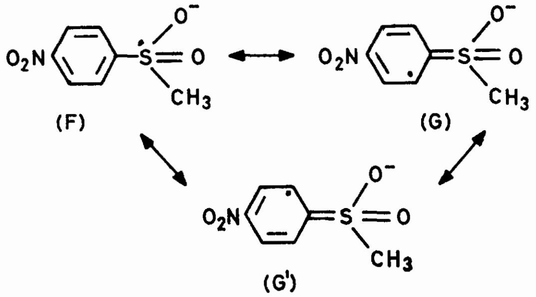
Relative ^1H n.m.r. contact shifts of the $Ni(acac)_2$ complexes of *para*-substituted anilines $NH_2C_6H_4X$

Substituent	*ortho*	*meta*	methyl
OMe	+1.00 [a]	−0.475	−0.097
SMe	+1.00	−0.453	−0.081
SOMe	+1.00	−0.470	−0.130
SO_2Me	+1.00	−0.507	−0.275

[a] Positive values represent downfield shifts corresponding to negative hyperfine splittings.


(D) (E)

On the other hand, in the *p*-methylsulphonyl nitroanion the 0.82 G methyl splitting suggests that the resonance structure mainly responsible for the non-zero spin density at sulphur is (F). The importance of mesomeric structures which place the negative charge on the sulphonyl oxygen atoms can also be inferred from the considerable decrease of the *meta*-splitting, with respect to nitrobenzene anion, which is due to partial neutralization of β spin density on these positions by α spin density from (G) and (G′). The same is true also for the *p*-methylsulphinyl derivative, even though the importance of structures like (F) and (G) is reduced. In the substituted phenyl nitroxides in which mesomeric forms similar to (F) and (G) cannot be written without separation of charge, the CH_3 splitting is much smaller than in the corresponding nitroanion for the *p*-sulphonyl derivative and undetectable in the *p*-sulphinyl compound. In the former case p_π–d_π interaction may also play some role in delocalizing the unpaired electron on the sulphur atom.[8]



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[7] K. Tori, Y. Yoshimura, and R. Muneyuki, *J. Amer. Chem. Soc.*, 1971, **93**, 6324.

[8] J. Goldman, T. E. Petersen, K. Torssell, and J. Becker, *Tetrahedron*, 1971, **29**, 3833.