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ESR studies of free radicals derived from hydroxyquinones

II *. Group 14 adducts of hydroxyanthraquinones and some phosphorus adducts of chrysazin

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Abstract

The reactions of Group 14 metal-centred radicals with 9,10-anthraquinone, 1,4-anthraquinone, and eight hydroxy-substituted 9,10-anthraquinones have been investigated by ESR spectroscopy. The results are discussed in terms of the regioselectivity of the addition reaction, the influence of hydroxyl substituents on the electron spin density distribution, and the effect of varying the Group 14 metal from silicon through to lead. 1,8-Dihydroxyanthraquinone (chrysazin) gives unusually persistent adducts with Group 14 metal-centred radicals and is also a spin-trap for phosphorus-centred radicals.

Introduction

Hydroxyanthraquinones are widespread in nature and have important applications as dyestuffs and pharmaceuticals [1]. The semiquinone radical anions and cations of these compounds have been extensively investigated by ESR [2] but neutral radicals derived from hydroxyanthraquinones have received less attention. An ESR spectrum attributed to the semiquinone radical derived from 9,10-anthraquinone (AQ) has been obtained by photolysis of the quinone in dioxane [3]; the 9-anthracenoxyl radical and some 10-substituted derivatives have been observed during the thermolysis or photolysis of bianthronyls and bianthrones [4]. Structur-

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* For Part I see ref. 8.

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ally related radicals are formed by the addition of silyl and other Group 14 metal-centred radicals to the carbonyl groups of quinones [5], a reaction which has been the subject of numerous ESR studies [6]. The substituted 9-anthracenoxyl radicals formed by addition of silyl, germyl and stannyl radicals to AQ were reported in 1978 [7]; the present paper deals with an extension of this study to include eight hydroxy-substituted anthraquinones and complements our recent work on hydroxynaphthoquinones [8]. Other published studies of structurally related species include radicals derived from xanthone, thioxanthone, and anthrone [9], and the 1,8-dihydroxy-9-anthron-10-yl radical [10].

Experimental

The quinones used in this work were all obtained commercially, as were the radical precursors triphenylsilane, triphenylgermane, hexabutyldistannane, tributylstannane, and hexaphenyldiplumbane. The quinones were purified by sublimation and/or recrystallisation. The radicals were generated as previously described [8]. The phosphorus radical adducts of chrysazin were also prepared by well established methods [11,12]. In a number of cases it was found possible to simplify the spectra by adding D_2O to the reaction mixture, thus causing collapse of the small doublet splittings due to hydroxyl protons.

Results and discussion

The coupling constants for all the radical adducts are collected in Tables 1 and 2. We first make a number of general observations and then deal with the results for each compound individually.

The effect of the metal

The variation in hyperfine coupling constants observed on descending the Periodic Table from Si to Pb is best illustrated by considering the adducts formed by AQ. The results are summarised in Fig. 1 where we have also included some published data [13] on radical-ion-pairs formed by alkali-metal reduction of AQ. The data nicely illustrate the effect on the spin distribution of increasing ionic character of the metal–oxygen bond. It has recently been established by TRIPLE * [14] and by experiments in liquid crystalline solvents [15] that the two coupling constants (a_1 0.53, a_2 0.97 G) in the free AQ radical anion have the same sign. As the perturbation by the metal atom increases, the coupling constants in positions 1 and 3 first decrease and then change sign, and the spin distribution approaches that of the odd alternant radical, 9-anthracenylmethyl.

Regioselectivity

When an organometallic radical adds to an unsymmetrically substituted anthraquinone such as alizarin there are two possible sites for radical addition. In the present investigation the observed radicals invariably correspond to formation of the least sterically hindered product, in general agreement with previous work [8,16].

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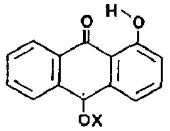
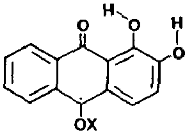
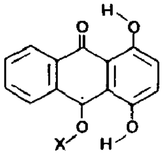
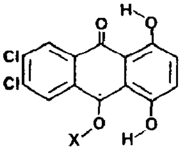
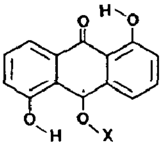
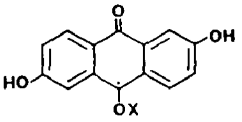
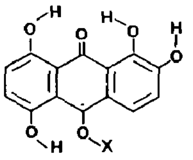
* TRIPLE = electron-nuclear triple resonance

Table 1

Hyperfine coupling constants (G) for some radical adducts of hydroxy-substituted 9,10-anthraquinones

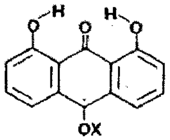
	X	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
	SiPh$_3$	0.66	3.94	0.90	3.94	2.60	0.20	2.90	0.77
	GePh$_3$	0.64	3.64	0.80	3.64	2.45	0.18	2.75	0.64
	SnBu$_3$	0.65	3.33	0.65	3.33	2.20	-	2.68	0.65
	SiPh$_3$	0.35	0.51	1.41	4.93	1.90	0.35	2.24	0.64
	GePh$_3$	0.30	0.50	1.25	4.60	1.75	0.30	2.20	0.50
	SiPh$_3$	0.33	4.55	0.65	-	2.25	0.50	2.60	0.65
	GePh$_3$	0.38	4.40	0.55	-	2.07	0.38	2.38	0.55
	SnBu$_3$	0.37	4.20	0.48	1.60	1.90	-	2.30	-
	SiPh$_3$	0.32	4.33	0.75	-	2.26	-	0.32	0.60
	GePh$_3$	0.33	4.26	0.69	-	2.05	-	0.30	0.40
	SiPh$_3$	0.45	3.65	0.83	3.62	-	0.45	3.05	0.18
	GePh$_3$	0.40	3.75	0.58	3.32	0.15	0.58	3.00	0.25
	SnBu$_3$	-	3.20	-	3.20	1.6?	-	3.20	-
	PbPh$_3$	0.25	2.85	0.25	2.60	1.18	0.25	1.18	-
	SiPh$_3$	0.45	-	1.05	2.90	2.95	-	2.80	0.70
	GePh$_3$	0.38	-	1.05	2.56	2.69	-	2.36	0.65
	SiPh$_3$	-	0.30	0.95	3.25	0.30	0.30	3.85	-
	GePh$_3$	-	0.28	0.88	3.08	-	0.28	3.68	-

1-Hydroxy-9,10-anthraquinone

Only weak signals were obtained by thermal reaction of this compound with Ph$_3$SiH, Ph$_3$GeH, or Bu$_3$SnH, but photolysis gave strong spectra which are consistent with addition to the unhindered carbonyl group. We were unable, however, to observe an ESR spectrum attributable to the lead adduct. The coupling constants,

Table 2

Hyperfine coupling constants (G) for some radical adducts of 1,8-dihydroxy-9,10-anthraquinone

	X	a_1	a_2	a_3	a_4	a_X
	H	0.16	3.47	0.64	3.47	1.12(^{1}H)
	$SiPh_3$	0.15	3.63	0.79	3.63	-
	$Si(SiMe_3)_3$	-	4.30	0.90	4.30	-
	$GePh_3$	0.15	3.50	0.66	3.50	-
	$SnBu_3$	-	3.20	0.50	3.20	42.54(^{117}Sn)
	$PbPh_3$	-	2.65	0.17	2.35	20.7(^{207}Pb)
	PPh_2	0.19	3.92	0.84	3.92	9.61(^{31}P)
	$P(OEt_2)_2$	-	3.47	1.03	3.47	9.99(^{31}P)
	$P(S)Et_2$	-	4.11	0.92	4.11	19.76(^{31}P)
	$P(O)Ph_2$	0.23	4.24	0.93	4.09	17.20(^{31}P)

obtained by computer simulation, are given in Table 1. They have been assigned on the basis of semi-empirical molecular orbital calculations and by comparison with related radicals, particularly the analogous adducts formed by 5-hydroxy-1,4-naphthoquinone (juglone) [8].

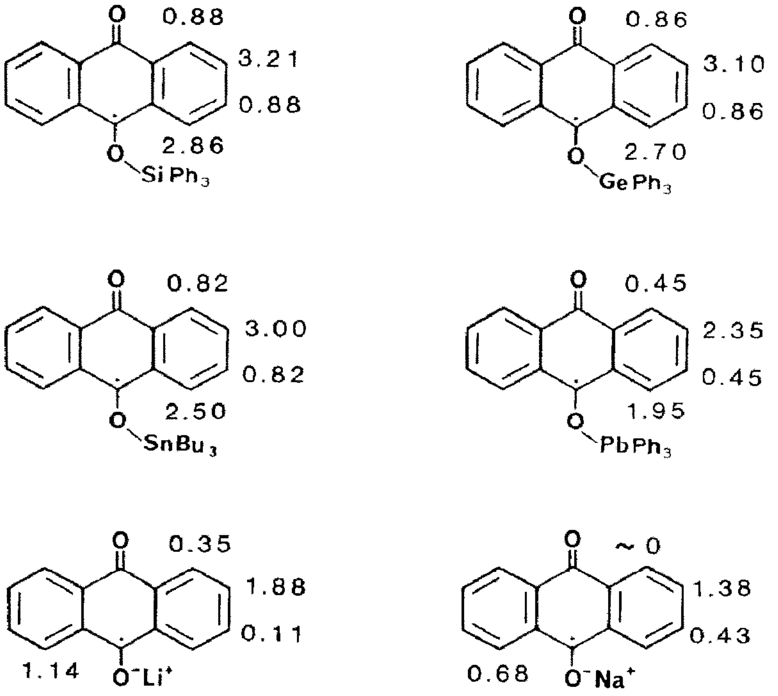


Fig. 1. The hyperfine coupling constants (G) of some radical adducts and radical ion-pairs of 9,10-AQ. Data from ref. 7, 13, and this work.

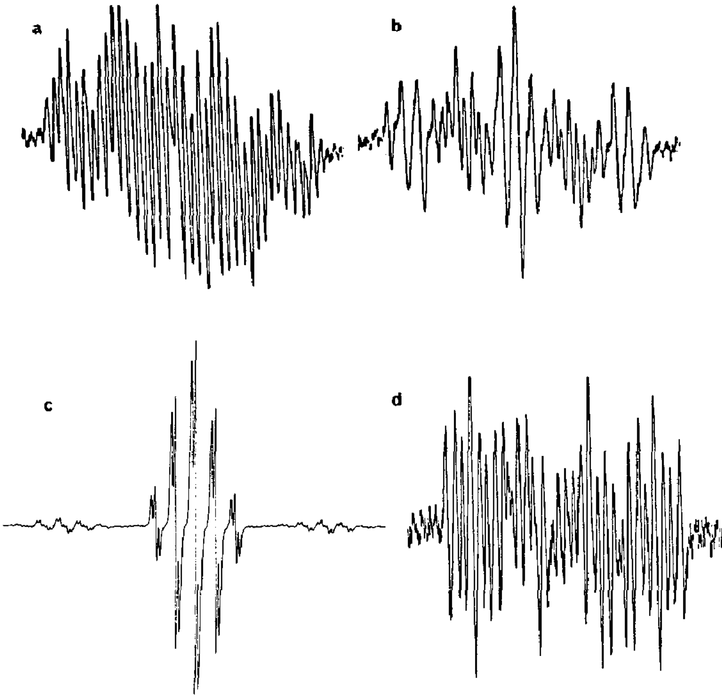


Fig. 2. (a) The ESR spectrum of the triphenylsilyl adduct of 1,4-dihydroxy-AQ recorded in t-butylbenzene at room temperature. (b) The same as in (a) but with the addition of a few drops of D_2O. (c) The tri-n-butyltin adduct of 1,8-dihydroxy-AQ. (d) The triphenylgermyl adduct of 2,6-dihydroxy-AQ.

1,2-Dihydroxy-9,10-anthraquinone (alizarin)

This compound reacted with both Ph_3SiH and Ph_3GeH in the melt but high temperatures (140 and 200°C, respectively) were required to obtain good ESR spectra. We were not able to obtain spectra attributable to the tin or lead adducts of alizarin.

The coupling constants of the silyl and germyl adducts in Table 1 are similar to those obtained for the 1-hydroxyquinone. The effect of the second hydroxy group on the spin distribution is to further localise the unpaired electron in the substituted ring. However, the major perturbation is due to the 1-hydroxy group.

1,4-Dihydroxy-9,10-anthraquinone (quinizarin)

Well resolved spectra of the triphenylsilyl adduct of quinazarin were obtained both in t-butylbenzene and in the melt. Addition of a few drops of D_2O to the former system led to the loss of one small doublet splitting (0.35 G) as shown in Fig. 2. It is not immediately obvious to which hydroxyl group this splitting should be assigned but comparison with related radicals suggest that it arises from the 1-OH group. We shall return to this point shortly. The triphenylgermyl adduct prepared in the melt has a similar pattern of coupling constants. However, photolysis of quinazarin in Bu_3SnH gave a strong, albeit short lived, spectrum with an additional 1.6 G doublet splitting. We were unable to obtain a lead containing adduct.

The additional doublet splitting in the stannyl adduct is just what we would expect for the 4-OH group; a similar coupling is found in the analogous radicals derived from naphthazarin [8]. The anomaly lies in the absence of a similar splitting in the silyl and germyl adducts. Such couplings are, however, known to be stereochemically and temperature dependent and we suggest that the 4-OH group has a different conformational preference in these species.

6,7-Dichloro-1,4-dihydroxy-9,10-anthraquinone

This quinone, which was included to aid in the assignment of the coupling constants obtained for quinizarin, gave the expected adducts on reaction with Ph_3SiH and Ph_3GeH in molten biphenyl, but only the radical anion was detected on mixing with tin or lead compounds. The coupling constants for the silyl and germyl adducts show that, as is usual, chlorine substitution has little effect on the spin distribution, although there is a shift in the *g*-value from 2.0038 to 2.0042. The replacement of the 2.6 and 0.5 G proton splittings in positions 6 and 7 by a 0.3 G quartet from a single chlorine nucleus is in accord with expectations. The magnitude of a chlorine coupling is normally about a tenth that of a proton in the same position, although opposite in sign [17].

The radicals formed on reaction with tin and lead compounds gave spectra consisting of a poorly resolved triplet (1.8–1.9 G). The hitherto unknown radical anion of the chloroquinone was prepared by electrochemical reduction in THF. The largest coupling was a triplet (1.83 G) with additional poorly resolved small splittings. The formation of the radical anion on reaction with tin or lead compounds can be ascribed to the effect of the chlorine substituents which increase the electron affinity of the quinone and favour an electron transfer mechanism.

1,5-Dihydroxy-9,10-anthraquinone (anthrarufin)

Photolysis of a melt of this quinone with triphenylsilane at 150 °C gave a strong well-resolved spectrum which could be readily analysed. The results obtained with Ge, Sn and Pb were less satisfactory and the coupling constants quoted in Table 1 should be treated with some circumspection. The spectrum of the germyl adduct contained a number of lines which could not be accounted for by computer simulation and that of the lead adduct was poorly resolved.

1,8-Dihydroxy-9,10-anthraquinone (chrysazin)

This compound proved to be the most effective spin trap of all the anthraquinones studied in this work. Some of the adducts were persistent for several weeks. Their coupling constants are summarised in Table 2.

At 80 °C a melt of Ph_3SiH and the quinone gave a strong ESR spectrum consisting of a quintet of triplets which we assign to the ring protons. At 140 °C a further small triplet from the hydroxyl protons was resolvable but the spectrum deteriorated rapidly at this temperature.

The triphenylgermyl adduct gave a very strong spectrum at 140 °C and it was possible to detect satellite lines with a 29.25 G doublet splitting in addition to the quintet of triplets of the main spectrum. The relative intensity of this spectrum was consistent with that expected for a single ^{13}C nucleus in natural abundance and we assign the splitting to the carbon atom in position 10. It is comparable in magnitude to the ^{13}C coupling constants reported for the triphenylsilyl and triphenylgermyl adducts of benzoyltriphenylsilane [18] and is indicative of slight non-planarity at the radical centre.

When chrysazin was dissolved in Bu_3SnH a spectrum was obtained within a few minutes of mixing. This was persistent for several days and became very strong when the solution was photolysed at 80 °C. Satellite lines from ^{119}Sn and ^{117}Sn are easily detectable (Fig. 2) and well resolved. The tin splittings are quite large (42.54 and 40.66 G) and suggest that the O–Sn bond has a preferred conformation orthogonal to the aromatic ring as is found in the analogous adducts of aromatic ketones [9,19].

The triphenyllead adduct, prepared by the photolysis of the quinone and Ph_6Pb_2 in t-butylbenzene, gave a quintet with broad lines which decayed within a few minutes.

A degassed solution of the quinone and tris(trimethylsilyl)silane in t-butylbenzene gave a spectrum, without photolysis, at room temperature soon after mixing. It was similar in appearance to that obtained with triphenylsilane but with slightly larger couplings. The spectrum grew in intensity with time and could still be recorded after one month. Photolysis of this system gave a strong complicated spectral pattern and a second species was distinguishable. This had a spectrum consisting of a quartet (4.2 G) of triplets (1.0 G) with the same g-value as the adduct. We assign this to a dimer since it has the same spectral parameters as the adduct with one large coupling missing. Semiquinone radicals are known to dimerise through the positions of highest spin density [20], presumably in this case positions 4 or 5 as they are less sterically hindered.

We have also investigated the trapping of phosphorus centred radicals by chrysazin. Thus photolysis of a solution of the quinone and tetraphenyldiphosphine in benzene at 298 K gave a spectrum with, in addition to the usual pattern of ring proton splittings, a 9.6 G doublet from ^{31}P. We assign this spectrum to the PPh_2 adduct. A similar spectrum observed on photolysis of a solution containing tetraethyl pyrophosphite and di-t-butyl peroxide is attributed to the $P(OEt)_2$ adduct. The adducts of the radicals $P(S)Et_2$ and $P(O)Ph_2$ derived from pentavalent phosphorus have rather larger ^{31}P splittings. The photoreaction of chrysazin with diphenyl phosphine, or dibenzyl phosphine, gave an ESR spectrum with only a small additional doublet splitting (ca. 1 G). We assign this to the hydrogen atom adduct since an identical spectrum was observed on photolysis of the quinone in THF.

The hyperfine couplings in the adducts derived from chrysazin are very similar to those reported for 1,8-dihydroxy-9-anthron-10-yl [10]. This radical, which has been implicated in the mode of action of the antipsoriatic drug dianthranol and its derivatives, has been the subject of several recent investigations, both in vitro [21] and in vivo [22].

2,6-Dihydroxy-9,10-anthraquinone (anthraflavic acid)

The silyl and germyl adducts of this quinone were prepared by photolysis in biphenyl at 145 °C, but we were unable to obtain the corresponding tin and lead radicals, probably because the compound is only sparingly soluble in THF and t-butylbenzene. The spectrum of the germyl adduct is shown in Fig. 2. The coupling constants (Table 1) indicate that hydroxyl substituents in the 2,6-positions exert only a small perturbation on the spin distribution.

1,2,5,8-Tetrahydroxy-9,10-anthraquinone (quinalizarin)

Quinalizarin may be regarded as a dihydroxy substituted chrysazin but does not show comparable reactivity or form persistent adducts. However, silyl and germyl adducts were formed after prolonged heating in biphenyl at temperatures as high as 200 ° C. Reactions with tin compounds gave a signal with a greater spectral width than the triphenylsilyl adduct, whereas the spectrum of the stannyl adduct would be expected to be narrower. We tentatively assign this spectrum to the radical anion.

1,4-Anthraquinone

This compound can be regarded as a substituted 1,4-naphthoquinone and we would expect a large doublet in the spectra of its adducts with Group 14 radicals. However, we were only able to obtain broad partially resolved spectra by reaction with silyl or germyl radicals. The spectral widths of ~ 12 G (Si) and ~ 10 G (Ge) are consistent with semi-empirical molecular orbital calculations which predict additional small splittings from six ring protons. The presence of many small doublet splittings would account for our inability to obtain well resolved spectra.

Reaction of 1,4-anthraquinone with tin or lead compounds gave spectra consisting of a 3.6 G triplet which we attribute to the radical anion. This assignment is supported by the observation that electrolytic reduction of the quinone in THF gave a well resolved spectrum with triplet splittings of 3.63, 0.55, and 0.28 G.

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