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Electron spin resonance spectra have been obtained from series of 2substituted anthrasemiquinones and of 3-substituted 1,8-dihydroxyanthrasemiquinones. The proton splittings are consistently assigned by means of linear correlation plots between splitting constants and a substituentdependent parameter. All lines in the plots of the two series of compounds obey the following linear equation

$$a_i^{\mathrm{R}} = A_i x^{\mathrm{R}} + a_i^{\mathrm{H}}$$

where  $a_i^{H}$  and  $a_i^{R}$  are the splitting constants at position *i* before and after the substituent has been added.  $A_i$  is the slope of the line for the splittings from position *i* and  $x^{R}$  is a constant characteristic of the substituent R.  $x^{R}$  is comparable to the Hammett  $\sigma$  parameter. Electron-donating substituents at C-2 are shown to increase the spin densities at the positions 1 > 6 > 8, and to decrease them at the positions 4 > 3 > 7 > 5, with the strength of the effect indicated. Electron-withdrawing substituents have the opposite effect. Preliminary Hückel molecular-orbital calculations qualitatively predict the observed correlations, solely by changing the parameter for the resonance integral.

Anthraquinones comprise the largest group of naturally occurring quinones, and practically all of them have non-symmetric substitution patterns.<sup>1</sup> Their e.s.r. spectra are complex, with many overlapping lines, in certain cases derived from more than eight different splitting constants. The constants range from a few mG to some G. The rules governing the spin distributions are largely unknown, and reliable assignments have been given only for few structures, mainly those with a symmetric substitution pattern.

Recently, we published spectra and data of a large number of anthrasemiquinones.<sup>2</sup> The present study is a continuation of this work, originally started as a search for correlations between e.s.r. splitting constants and other molecular properties. We have been especially interested in examining related series of anthrasemiquinones in which a single substituent is varied in order to obtain information about the redistributions of spin densities within the three-ring radical skeleton. In addition, we hoped to obtain rules for obtaining unique assignments and for predicting spectra of previously unstudied compounds.

In this paper we present the results we have obtained from considering 11 suitable model compounds, partly a series of monosubstituted anthraquinones, partly a series containing in addition the 1,8-dihydroxy grouping. We have focused attention on the effects from substituents added at  $\beta$ -positions with no neighbours. This is in order to avoid complications and unknown factors due to steric hindrance, as observed for substituents at  $\alpha$ -positions.<sup>3</sup>

#### Experimental

The anthrasemiquinone radicals were generated in alkaline aqueous ethanol at room temperature by reducing the corresponding anthraquinones with sodium dithionite. The

			$a_i^{\mathbf{R}}/\mathbf{G}$							
R	$x^{\mathrm{R}}$	σ	2	4	5	6	7			
$O^-$ Me H $CO_2^-$	$-0.670 \\ -0.096 \\ 0 \\ 0.143$	$-0.52 \\ -0.17 \\ 0 \\ 0.13$	0.556 1.414 1.577 1.768	3.093 1.435 1.192 0.812	1.663 1.261 1.192 1.085	0.623 0.937 0.980 1.049	2.240 1.680 1.577 1.428			

 Table 1. E.s.r. proton splitting constants for some 3-substituted

 1,8-dihydroxyanthrasemiquinones

For numbering positions see fig. 1.  $\sigma$  parameters are from ref. (7); for the  $x^{\text{R}}$  parameters see text. A splitting constant of 0.996 G is observed from the methyl-group protons.

solvent composition was *ca*. 64% alcohol (v/v). 1-[<sup>2</sup>H]anthraquinone was synthesized electrolytically from 1-bromoanthraquinone.

The spectra were recorded on a Bruker ER 200 spectrometer with a modulation frequency of 12.5 or 25 kHz and a modulation amplitude of 25 mG or less. The microwave power was kept below 0.3 mW to avoid saturation effects. All digitized spectra (4 k, with a resolution of 2.5 mG) were simulated on a Vax 11/780 computer, and 'best-fit' parameters were obtained by an iterative optimization procedure as described previously.<sup>4</sup>

## **Results and Discussion**

A crucial point in following how unpaired spin is redistributed owing to the addition of a substituent is to have available reference compounds with spectra correctly interpreted and splitting constants uniquely assigned. For anthrasemiquinones this is not a trivial problem because of the many inherent splitting constants (often of similar magnitude) for each individual compound.

In order to assign the two splittings of anthrasemiquinone, we have synthesized 1-[<sup>2</sup>H]anthraquinone. We obtain the unambiguous result 0.550 and 0.960 G for the  $\alpha$ - and  $\beta$ -splittings, respectively.<sup>2</sup>

1,8-Dihydroxyanthrasemiquinone is a key compound in the present study. Of the four splitting constants observed the one from the hydroxyl protons is revealed immediately by deuterium exchange. For the remaining splittings (0.980, 1.192, 1.577 G) the published assignments are conflicting.<sup>5,6</sup> From the literature and the available evidence there seems no doubt that the larger splitting has to be assigned to the proton at C-2, with an identical one derived from C-7. An assignment by additivity indicated the result  $a_2 > a_3 > a_4$ , under the assumption that introduction of a hydroxyl group at an  $\alpha$ -position had the same effect, whether or not the quinonoid oxygens already participated in internal hydrogen bonds.<sup>3</sup> From what follows this assignment turns out to be incorrect and in obvious conflict with the result from 1,8-dihydroxy-3-methylanthrasemiquinone, viz. the methyl group at C-3 yields a proton splitting of 0.996 G, comparable to a splitting of 0.980 G from the unsubstituted position of the parent semiquinone (table 1). We here use the assumption, borne out by many experiments, that methyl-group protons give rise to a splitting of comparable magnitude to the splitting of the C-H proton at the site of substitution. Thus, we shall assume the assignment  $a_2 > a_4 > a_3$ , cf. ref. (6).

## 3-Substituted 1,8-Dihydroxyanthrasemiquinones

We shall begin discussing how the correlation plot of fig. 1 is obtained. It is obvious that splitting constants change considerably, and are dependent on the applied substituent



Fig. 1. The change in the ring-proton splitting constants of 3-substituted 1,8-dihydroxyanthrasemiquinones vs. the substituent parameter  $x^{R}$ . For a definition of  $x^{R}$  see text. The open symbols on the lines have a size of 30 mG.

	R	<i>a</i> <sub>1</sub> <sup>OH</sup>	<i>a</i> <sup>OH</sup> <sub>8</sub>
он о но	O-	0.138	0.156
7	Me	0.185	0.185
6 R	Н	0.195	0.195
0_	$\mathrm{CO}_2^-$	0.219	0.213

**Table 2.** E.s.r. hydroxyl-proton splitting constants (G) for some 3-substituted 1,8-dihydroxyanthrasemiquinones

(table 1). The question is whether simple expressions exist, which correlate the observed behaviour. Attempts to find parameters for the various substituents correlating our data led to plots with scattered points, exhibiting no clear trends. The only plot of some interest is a 'Hammett plot' of splitting constants  $vs. \sigma$  parameters.<sup>7</sup> In short we have followed a different approach.

A first step is to make out where the spin density increases and where it decreases when

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position	$A_{i}$	$a_i^{\scriptscriptstyle \mathrm{H}}$	$a_i^{ m O}$	r	$\sigma(a_i^{\mathrm{R}})$	$\sigma(a_i^{\scriptscriptstyle \mathrm{H}})$	$\sigma(A_i)$
2	1.500	1.562	1.577	1.000	13	7	20
4	-2.822	1.194	1.192	-1.000	27	15	43
5	-0.708	1.190	1.192	-1.000	4	2	6
6	0.528	0.980	0.980	0.999	7	4	12
7	-0.994	1.576	1.577	-1.000	7	4	12

 Table 3. Parameters obtained in the linear-regression analysis of the data from table 1 (cf. fig. 1)

 $a_i^{\rm R} = A_i x^{\rm R} + a_i^{\rm H}$ .  $A_i$ ,  $a_i^{\rm H}$  and  $a_i^{\rm O}$  are in G, the standard deviations in mG. The unsubstituted constants  $a_i^{\rm O}$  are shown for comparison.

Table 4. E.s.r. proton splitting constants for some 2-substituted anthrasemiquinones

R	$x^{R}$	σ	1	4	5	8	3	6	7
0-	-0.670	-0.52	1.959	0.147	0.271	1.030	0.537	1.615	0.610
NH。	-0.430	-0.66	1.443	0.248	0.401	0.897	0.556	1.411	0.679
OMe	-0.287	-0.27	1.071	0.307	0.335	0.778	0.731	1.226	0.781
Et	-0.067	-0.15	0.698	0.507	0.509	0.591	0.853	1.034	0.930
Н	0	0	0.550	0.550	0.550	0.550	0.960	0.960	0.960
Cl	0.096	0.23	0.353	0.609	0.561	0.487	1.070	0.839	0.978
$\operatorname{CO}_2^-$	0.143	0.13	0.259	0.633	0.611	0.445	1.095	0.824	1.012

For numbering positions see fig. 3 and 4.  $\sigma$  parameters are from ref. (7); for the  $x^{R}$  parameters, see text. Additional splitting constants (G) are as follows: NH<sub>2</sub> ( $a_{N} = 0.337$ ,  $a_{NH_2} = 0.073$ ); Et ( $a_{CH_2} = 0.705$ ).

a substituent is added, say, at C-3 of 1,8-dihydroxyanthrasemiquinone. Conclusive evidence comes from examining the data of table 2, showing the hydroxyl-proton splittings of four representative compounds. The splittings are definitely derived from the hydroxyl protons, as substantiated by deuterium exchange in heavy water. Considering the individual splittings we observe that electron-donating groups, O<sup>-</sup> and Me, cause a decrease in the magnitude of the splitting constants, *i.e.* a decrease at positions 1 and 8. For an electron-withdrawing group,  $CO_2^-$ , we observe the opposite effect. O<sup>-</sup> has the strongest effect, and Me and  $CO_2^-$  have effects of similar strength, but of opposite sign. These trends have obvious similarities to the Hammett  $\sigma$  parameters,<sup>7</sup> and have led us to define a substituent parameter  $x^{R}$  as follows:

$x^{R} = 0;$	for $\mathbf{R} = \mathbf{H}$
$x^{\mathbf{R}} > 0;$	for electron-withdrawing groups
$x^{\mathbf{R}} < 0;$	for electron-donating groups
$x^{0^-} = -0.67;$	arbitrarily chosen.

To fix new  $x^{R}$  parameters for other substituents we begin by making a plot of the splitting constants of the compounds with R = H and  $R = O^{-} vs$ . their  $x^{R}$  parameters defined above. The two sets of points are placed on vertical lines above  $x^{H} = 0$  and  $x^{O^{-}} = -0.67$ . We then connect the three and five points with five straight lines under the assumption that a linear relation exists between splitting constants and the  $x^{R}$  parameters. Since we do not know the assignment for the  $R = O^{-}$ -substituted compound, a set of lines can be drawn in 30 different ways. However, we can obtain the 'correct' set if we add to vertical lines the five splittings of the  $CO_{2}^{-}$ -substituted compound and



Fig. 2. The e.s.r. spectrum of 2-aminoanthrasemiquinone. The outermost 1:2:1 triplets are from the NH<sub>2</sub> protons. The spectrum was simulated with the data of table 4 and a linewidth of 0.074 G.

those of the Me-substituted analogue and move the points in the positive and the negative directions from  $x^{\rm H} = 0$ , respectively. We then find that all points plotted fall on straight lines in one case only out of the 30 possible. This case is shown in fig. 1. We have obtained a linear correlation plot with four points on each line. Since we know the assignments of the splitting constants for the unsubstituted compound we have assigned all splitting constants of table 1, with the exception of distinguishing between the  $\beta$ -protons 2 and 7, and  $\alpha$ -protons 4 and 5. However, taking recourse to a study of the non-symmetric 1-hydroxy-6-methoxy- and 1-hydroxy-7-methoxy-anthrasemiquinones and other methoxy-substituted anthrasemiquinones, the assignment of table 1 turns out to be the only consistent one. These results will be published in a forthcoming paper.

The lines in the correlation plot can be represented by the following expression:

$$a_i^{\rm R} = A_i x^{\rm R} + a_i^{\rm H}$$

where  $a_i^{\rm R}$  and  $a_i^{\rm H}$  are the splitting constants from position *i* of 1,8-dihydroxyanthrasemiquinone, with and without the substituent R at C-3.  $A_i$ , the slope of line *i*, is a sole function of the proton position. Concerning the  $x^{\rm R}$  parameters determined above, we observe them to be comparable to the Hammett  $\sigma$  parameters in the scale we have chosen (table 1).

From a regression analysis we obtain the results of table 3. The extreme linearities are reflected in the correlation coefficients, with  $|\sigma| \ge 0.999$  throughout, and in the standard deviations shown in mG. The experimental uncertainties in the splitting constants are estimated to be less than 20 mG.

#### 2-Substituted Anthrasemiquinones

Turning to the monosubstituted anthrasemiquinones, we have performed a similar analysis for seven compounds, the data of which are shown in table 4. Most monosubstituted anthrasemiquinones have very complex e.s.r. spectra. Fig. 2 shows as



Fig. 3. The change in the  $\alpha$ -proton splittings of 2-substituted anthrasemiquinones vs. the substituent parameter  $x^{R}$ , cf. fig. 1.

an example the spectrum of 2-aminoanthrasemiquinone, which may be analysed in terms of nine splitting constants, ranging from 0.073 to 1.443 G. The 1152 lines are confined within 6.455 G.

Plots of the  $\alpha$ - and  $\beta$ -proton splitting constants vs.  $x^{R}$  are shown in fig. 3 and 4, respectively. The figures have been made by first plotting the data for the three semiquinones with no substituent, with the O<sup>-</sup>, and with the CO<sub>2</sub> substituent, using the previously obtained  $x^{R}$  values. In order to determine new substituent parameters we add in turn the data of the four remaining semiquinones, using the same procedure as described in obtaining fig. 1. We obtain best agreement by using the same  $x^{R}$  value in both figures. Furthermore, all eight  $x^{R}$  values (tables 1 and 4) compare well with the Hammett  $\sigma$  parameters.

From fig. 3 and 4 an excellent linearity for the proton splittings vs.  $x^{R}$  for the positions 1, 6, 7 and 8 appears, and a reasonable linearity for the positions 3, 4 and 5. The data points are somewhat scattered for the latter three positions, but clear trends with positive slopes are obvious for all three matching lines.

The results of the regression analysis are shown in table 5. The correlation coefficients and the standard deviations stress the excellent agreement to linearity, for nearly all seven lines. A TRIPLE resonance study on 2-hydroxyanthrasemiquinone revealed a negative spin density for one of the carbon positions, yielding a splitting constant of +0.147 G from the corresponding proton.<sup>3</sup> Since we have applied numerical values to all splitting constants in the present work, this particular splitting has been given the value -0.147 G in fig. 2. The opposite sign for the splitting would give a much better



Fig. 4. The change in the  $\beta$ -proton splittings of 2-substituted anthrasemiquinones vs. the substituent parameter  $x^{\text{R}}$ , cf. fig. 1.

fit for line 4, cf. the comment to table 5. However, we still obtain a consistent assignment for all splittings of the seven compounds studied and have been unable to check the result of negative spin density owing to lack of 2-hydroxyanthraquinone.

We can generalize the total results for both series as follows:



R electron - donating

R electron - withdrawing

Here + and - mean the spin densities increase and decrease, respectively, when R is substituted at C-2. The relative power of a particular substituent to redistribute the unpaired spin is expressed through its  $x^{R}$  value, whereas the magnitude and direction of change of unpaired spin at a particular position is given by the slopes  $A_i$ , cf. tables 3 and 5.

As mentioned earlier, we have used throughout the incorrect but customary practice of considering proton splitting constants as positive for positive spins. In choosing the opposite convention the signs of the  $A_i$  parameters should be changed accordingly.

## **Molecular-orbital Calculations**

In order to obtain some insight into the trends observed for the two series of anthrasemiquinones studied, we have performed preliminary calculations on 2-

position	$A_{i}$	$a_i^{\scriptscriptstyle \mathrm{H}}$	$a_i^{\mathrm{O}}$	r	$\sigma(a_i^{\mathrm{R}})$	$\sigma(a_i^{\scriptscriptstyle \mathrm{H}})$	$\sigma(A_i)$
1	-2.071	0.545	0.550	-0.999	34	15	46
$4^a$	0.906	0.544	0.550	0.979	62	28	84
5	0.406	0.533	0.550	0.951	43	19	59
8	-0.740	0.554	0.550	-0.998	16	7	22
3	0.743	0.958	0.960	0.970	61	27	83
6	-0.999	0.957	0.960	-0.998	19	8	25
7	0.527	0.941	0.960	0.990	24	11	33

Table 5.	Parameters	obtained in	the	linear-regression	analysis	of tl	he data	of	table	4 (cf	fig.	3
				and 4)								

<sup>*a*</sup> For an explanation see text and table 3. The figures for position 4 are based on the data of table 4 with one negative constant (-0.147). If +0.147 is used we obtain the following figures shown in the same order as above: (0.635, 0.539, 0.550, 0.990, 29, 13, 40).

substituted anthrasemiquinones, using the simple Hückel molecular-orbital (HMO) method. For the quinonoid oxygens we have used the parameters  $h_0 = 2.1$  for the Coulomb integral and  $k_{co} = 1.85$  for the resonance integral. High values are chosen in order to incorporate the influences from the polar solvent on the effective electronegativity of the oxygen atoms. We have not at this stage attempted to determine 'best values' for these parameters, since the crudity of the HMO method only allow us to use it in a qualitative manner.

A calculation for anthrasemiquinone yields the spin densities  $\rho_1 = 0.0300$  and  $\rho_2 = 0.0452$ , corresponding to  $a_1 = 0.59$  G and  $a_2 = 0.90$  G, with a Q value (numerical) of 19.8 G applied in the McConnell equation.  $a_1$  and  $a_2$  compare well with the experimental  $a_1 = 0.55$  G and  $a_2 = 0.96$  G (table 4) for the unsubstituted compound.

We next add a hypothetical substituent R at C-2, contributing two  $\pi$ -electrons. Gendell *et al.*<sup>8</sup> have put forward a simple model based on the HMO method, accounting for the variation of splitting constants with solvent in the semiquinone ions. In their calculations they used a larger  $h_0$  parameter from the Coulomb integral in polar and protic solvents than in less polar and aprotic solvents. Along with this, and since we are dealing with only one polar solvent system, we have chosen a large  $h_R$  and kept it constant on the value  $h_R = h_0 = 2.1$ . The changes of substituents are then reflected solely by a change in the parameter for the resonance integral for R. We have performed eight calculations, varying  $k_{CR}$  from 0.4 to 1.8 in steps of 0.2. A plot (not shown) of the spin densities in the eight calculations for the seven actual carbon positions vs. the  $k_{CR}$  parameters yields seven nearly linear curves with positive and negative slopes, in agreement with the slopes of the lines of fig. 3 and 4 to the left of  $x^H = 0$ . Using the HMO energy for the single occupied orbital instead of the  $k_{CR}$  parameter in the plot led to better linearities for the seven lines, *viz*. correlation coefficients of |r| > 0.970, apart from line 7 which had r = 0.955.

The actual slopes obtained, using MO energies on the x-axis, are as follows with the first figure being from table 5 and the second from the calculations:

The two sets of data have been scaled to make the slope for line 1 identical.

It makes little sense to try to obtain detailed agreement by varying the Hückel parameters owing to the approximations inherent the HMO method. However, since we are dealing with molecules of a very similar type, it may not be unreasonable to expect

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that the calculations indicate the main features of the variation in ring proton splittings from a change of substituent.

## Conclusions

E.s.r. measurements on two series of anthrasemiquinones have shown that substituents added at C-2 can be arranged in an order which reflects that they perturb the spin distributions for all other ring positions in a linear fashion. The linear correlations of splitting constants vs. constants characteristic of the substituents show strong resemblance to correlations obeyed by the Hammett equation. If we consider benzene derivatives of the type  $C_6H_4XY$ , where Y is a proton or a side-chain being subject to the perturbation from the variable substituent X, the Hammett equation takes the form

$$\log k = \rho \sigma + \log k^{\circ}$$
.

Here k and  $k^{0}$  are the rate constants of some specified reaction for the substituted and the unsubstituted compound, respectively.  $\sigma$  is a constant characteristic of a given substituent X and  $\rho$  is a constant characteristic of the 'position' of side-chain Y and the same for all substituents X. The equation from the present e.s.r. study takes the form

$$a_i = A_i x + a_i^0$$

where  $A_i$  has the same meaning as  $\rho$  and x has the same meaning as  $\sigma$ .  $a_i$  and  $a_i^{O}$  are the splitting constants from position *i* after and before substitution. In the application of the Hammett equation different  $\sigma$  values are required for different molecular positions (the *para/meta-ortho* problem), whereas in the e.s.r. equation only one set of x values for the various substituents is required to correlate the behaviour of splittings for all seven ring positions of  $\beta$ -substituted anthrasemiquinones. A natural question to ask is whether the e.s.r. correlation equation is applicable to other pertinent radical systems *e.g.* naphthosemiquinones substituted at C-6. Consideration of three systems we have available ( $\mathbf{R}_6 = \mathbf{Me}, \mathbf{O}^-, \mathbf{H}$ ),<sup>2</sup> indicates this to be the case, however, with different slopes,  $A_i$ , as one would expect, but unchanged  $x^{\mathbf{R}}$  values.

Looking at table 4 and comparing x and  $\sigma$  values, a change in the order appears for the couples O<sup>-</sup>/NH<sub>2</sub> and for Cl/CO<sub>2</sub><sup>-</sup>. Since O<sup>-</sup> and CO<sub>2</sub><sup>-</sup> are the only substituents in the table with a formal charge, different counter-cations and/or different pH values in the experimental set-up for the present study and for the ones furnishing the  $\sigma$  values might lead to a simple explanation of the discrepancies.

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