Steric Effects observed in the Electron Spin Resonance Spectra of Some Arylsemiquinones

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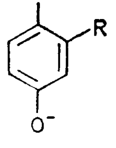
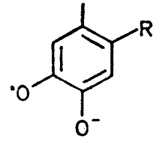
The e.s.r. spectra of radicals derived from arylhydroquinones are discussed with particular reference to how the conformations of the radicals vary with increasing *ortho*-substitution on the aryl group. With two *ortho*-substituents the dihedral angle becomes close to 90° so that the major splitting from the aryl group is from the *meta*-protons. The results are rationalised in terms of two contributions to the coupling constants of protons associated with the aryl group, one from the π electron system and the other from delocalisation through the σ bond framework.

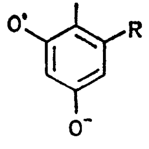
THE mechanism of the initial stages in the autoxidation of hydroquinones has recently been elucidated by means of e.s.r. spectroscopy.[1] After initial formation of the appropriate semiquinone (I) the reaction later involves secondary radicals of types (A) and (B).



(I)



(A)



(B)

The e.s.r. spectra of these three species are related to each other in a simple way and so it is useful to be able to obtain three spectra from each starting material, since they corroborate each other and aid us in the assignments of coupling constants. In a previous paper we discussed radicals from *para*-substituted arylhydroquinones.[2] Trends were pointed out both in the hyperfine splittings of protons attached to the semiquinone ring, and in those of protons in the aryl fragment. The results indicated that delocalisation of spin density *away* from the semiquinone ring is facilitated by electron-donating groups in the *para*-position of the attached aryl group.

Other things being equal, we would have expected similar trends when the substituents were in an *ortho*- instead of the *para*-position.

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[1] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, 1130.

[2] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, **2264**.

RESULTS

However, as regards the coupling constants on the semiquinone ring, the effects of *ortho*-substituents in the aryl group are much smaller than when those substituents are in the *para*-position, and are roughly the same as in the corresponding *meta*-derivatives (see Tables 1 and 2).

This last observation can be coupled with the more striking result, that the coupling constants of the aryl protons are about twice as large when a substituent is either in the *meta*- or *para*-position than when it is *ortho* with respect to the bond joining the two rings.

These two broad generalisations have led us to investigate more closely how changes in the dihedral angle affect the coupling constants of protons in the system which give a measure of the conjugation between the two rings.

A number of additional points arise from the results given in Tables 1 and 2 and require explanation. (1) Whereas the *meta*-proton coupling constants seem to remain constant with increasing *ortho*-substitution on the aryl group, the *ortho*- and *para*-splittings decrease sharply. (2) For methyl substituents on the aryl group (i) *p*-methyl proton splittings are about the same as those of *p*-hydrogens, (ii) *o*-methyl proton splittings are less than those of *o*-hydrogens, and (iii) *m*-methyl proton splittings are about half those of *m*-hydrogens. (3) Related to points in (2), when the aryl group has two *o*-methyl groups, a *p*-chloro or -methyl group does not affect the resolution. On the other hand in the *o*-chlorophenylsemiquinone the aryl proton splittings are not resolved (due probably to broadening by hyperfine coupling with ^{35}Cl and ^{37}Cl nuclei). (4) In the primary radicals (I), *no* splitting is observed from *o*-methyl protons, from *o*-nitro nitrogen nuclei, or from ^{19}F on the *meta*-position.

Most of these points can be explained in terms of the increase in dihedral angle between the two rings when the number of *ortho*-substituents is increased.

TABLE 1

(a) Coupling constants of primary radicals from mono-substituted arylsemiquinones

	Coupling constants (G)						
				Aryl group splittings			
Aryl group	a_3	a_5	a_6	$a_o(H)$	$a_m(H)$	$a_p(H)$	$a_{substituent}$
Ph	1·99	2·56	2·12	0·27	0·16	0·27	
o-FC_6H_4	2·07	2·52	2·21	0·16	0·16	0·16	$a_F = 0·56$
m-FC_6H_4	2·02	2·56	2·13	0·28	0·15	0·28	$a_F \approx 0·04$ *
p-FC_6H_4	2·01	2·54	2·12	0·28	0·15		$a_F = 0·57$
o-ClC_6H_4	2·12	2·52	2·22	†			
o-BrC_6H_4	2·10	2·50	2·20	0·10	0·10	0·10	
p-BrC_6H_4	2·04	2·48	2·04	0·28	0·16		
o-MeC_6H_4	2·09	2·51	2·20	0·13	0·13	0·13	$a_{Me} \approx 0·05$ *
m-MeC_6H_4	1·96	2·58	2·14	0·27	0·18	0·27	$a_{Me} = 0·09$
o-$OMeC_6H_4$	2·05	2·63	2·17	0·15	0·15	0·15	
m-$OMeC_6H_4$	2·02	2·54	2·05	0·26	0·15	0·26	
o-OHC_6H_4	1·82	2·65	2·28	0·14	0·14	0·14	
m-OHC_6H_4	1·81	2·57	2·17	0·26	0·15	0·26	
p-OHC_6H_4	1·38	2·53	2·33	0·32	0·14		
o-$NO_2C_6H_4$	2·10	2·56	2·10	0·16	0·16	0·16	$a_N \approx 0·06$ *
m-$NO_2C_6H_4$	2·26	2·44	1·94	0·27	0·17	0·27	$a_N \approx 0·04$ *
p-$NO_2C_6H_4$	2·38	2·50	1·92	0·30	0·15		$a_N = 0·07$
o-PhC_6H_4	2·06	2·60	2·06	†			

* Unresolved splitting, estimated from observed splitting in secondary (A). † Aryl group splittings not resolved.

(b) Coupling constants of secondary radicals from monosubstituted arylsemiquinones

	Coupling constants (G)											
	Secondary radical (A)						Secondary radical (B)					
			Aryl group splittings						Aryl group splittings			
Aryl group	a_3	a_6	$a_o(H)$	$a_m(H)$	$a_p(H)$	$a_{substituent}$	a_3	a_5	$a_o(H)$	$a_m(H)$	$a_p(H)$	$a_{substituent}$
Ph	0·50	1·08	0·54	0·31	0·54		0·67	4·52	0·12	0·12	0·12	
o-FC_6H_4	*						0·68	4·72	†			$a_F = 0·40$
m-FC_6H_4	0·53	1·15	0·53	0·28	0·53	$a_F = 0·08$	0·66	4·64	0·12	0·12	0·12	
p-FC_6H_4	0·51	1·09	0·58	0·30		$a_F = 1·09$	0·66	4·48	0·12	0·12		$a_F = 0·24$
o-ClC_6H_4	0·50	1·27	0·25	0·25	0·20		0·65	4·72	†			
o-BrC_6H_4	0·48	1·23	0·24	0·24	0·17		0·64	4·74	†			
p-BrC_6H_4	0·49	1·13	0·59	0·31			0·67	4·56	0·12	0·12		
o-MeC_6H_4	0·51	0·96	0·28	0·28	0·28	$a_{Me} = 0·11$	0·64	4·56	†			
m-MeC_6H_4	0·52	1·06	0·52	0·32	0·52	$a_{Me} = 0·16$	0·65	4·45	0·12	0·12	0·12	
o-$OMeC_6H_4$	0·52	1·12	0·26	0·26	0·26		0·67	4·65	†			
m-$OMeC_6H_4$	0·54	1·08	0·54	0·29	0·54		0·68	4·56	0·12	0·12	0·12	
o-OHC_6H_4	0·49	0·82	0·24	0·24	0·30		0·64	4·16	†			
m-OHC_6H_4	0·51	0·96	0·51	0·27	0·51		0·66	4·36	0·12	0·12	0·12	
p-OHC_6H_4	0·53	0·53	0·65	0·27			0·63	4·00	0·14	0·10		
o-$NO_2C_6H_4$	*					$a_N = 0·13$	‡					
m-$NO_2C_6H_4$	0·43	1·42	0·60	0·30	0·60	$a_N = 0·09$	‡					
p-$NO_2C_6H_4$	0·45	1·48	0·60	0·30		$a_N = 0·15$	0·70	4·86	0·12	0·12		
o-PhC_6H_4	0·48	1·04	0·30	0·30	0·20	0·10 (2 protons)	0·64	4·44	†			

* Spectra not analysed. † Aryl group splittings not resolved. ‡ Spectra not obtained.

THEORY

It is not difficult to find a relatively simple, satisfactory model for the situation presented by two rings joined together. In the first place it seems that the coupling constants in the three types of radical bear a simple relationship to each other, *i.e.* the hyperfine splittings of methyl or aryl protons which are associated with the aryl substituents vary in the same way for all three types of radical, as far as one can detect. These splittings in radicals of type (B) are about half those in the corresponding primary radicals which in turn are about half those in the radicals of type (A).

TABLE 2

(a) Coupling constants of primary radicals from polysubstituted arylsemiquinones

	Coupling constants (G)						
				Aryl group splittings			
Aryl group	a_3	a_5	a_6	a_o(H)	a_m(H)	a_p(H)	$a_{\text{substituents}}$
α-Naphthyl	2·16	2·52	2·16			0·10 (2 protons) 0·16 (1 proton)	
2-Me, 3-ClC_6H_3	2·20	2·52	2·20	*			
2,3-$Me_2C_6H_3$	2·05	2·52	2·18	0·12	0·12	0·12	
2,4-$Me_2C_6H_3$	2·05	2·55	2·18	0·13	0·13		$a_{Me(o)}$ = 0·13
2,5-$Me_2C_6H_3$	2·05	2·55	2·17	0·12	0·12	0·12	
2,6-$Me_2C_6H_3$	2·10	2·50	2·26		0·15		$a_{Me(o)}$ ~ 0·05 †
2-Me,6-ClC_6H_3	2·14	2·50	2·18		0·13		
2,6-$Cl_2C_6H_3$	2·10	2·50	2·42		~0·10		
2,6-Me_2,4-ClC_6H_2	2·20	2·48	2·20		0·15		$a_{Me(o)}$ ~ 0·05 †
2,6-Me_2,4-BrC_6H_2	2·20	2·49	2·20		0·14		$a_{Me(o)}$ ~ 0·05 †
2,4,6-$Me_3C_6H_2$	2·11	2·54	2·26		0·16		$a_{Me(o)}$ ~ 0·04 †
2,4,6-Me_3, 3-BrC_6H	2·16	2·50	2·16		0·11		

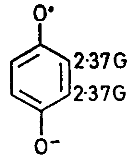
* Aryl group splittings not resolved. † Unresolved splitting, estimated from observed splitting in secondary (A).

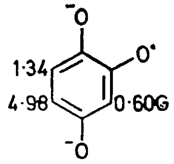
(b) Coupling constants of secondary radicals from polysubstituted arylsemiquinones

	Coupling constants (G)											
	Secondary radical (A)						Secondary radical (B)					
			Aryl group splittings						Aryl group splittings			
Aryl group	a_3	a_6	a_o(H)	a_m(H)	a_p(H)	$a_{\text{substituent}}$	a_3	a_5	a_o(H)	a_m(H)	a_p(H)	$a_{\text{substituent}}$
α-Naphthyl	0·53	1·16				0·23 (2 protons) 0·34 (1 proton)	0·64	1·60	†			
2-Me, 3-ClC_6H_3	*						0·64	4·64	†			
2,3-$Me_2C_6H_3$	0·48	1·10	0·24	0·24	0·24		0·64	4·48	†			
2,4-$Me_2C_6H_3$	*					$a_{Me(o)}$ = 0·10	0·64	4·52	†			
2,5-$Me_2C_6H_3$	*						0·64	4·52				
2,6-$Me_2C_6H_3$	0·51	1·08		0·31		$a_{Me(o)}$ = 0·09	0·63	4·52		0·08		
2-Me, 6-ClC_6H_3	0·54	1·18		0·30			0·56	5·86	†			
2,6-$Cl_2C_6H_3$	0·54	1·38		0·27			1·20	5·16	†			
2,6-Me_2, 4-ClC_6H_2	0·51	1·08		0·30		$a_{Me(o)}$ = 0·09	0·63	4·62	†			
2,6-Me_2, 4-BrC_6H_2	0·50	1·09		0·30		a_{Me} = 0·09	0·64	4·62	†			
2,4,6-$Me_3C_6H_2$	0·49	1·00		0·32		$a_{Me(o)}$ = 0·08 $a_{Me(p)}$ ~ 0·00	0·65	4·52		0·09		
2,4,6-Me_3, 3-BrC_6H	*						0·64	4·60	†			

* Spectra not analysed or resolved. † Aryl group splittings not resolved.

This suggests first that the dihedral angle is probably the same in all three cases and secondly, that the splittings in the aryl group are roughly proportional to the spin density on the carbon atom to which they are attached. Support for this second possibility comes from the coupling constants in semiquinone itself and the radical from 1,2,4-trihydroxybenzene, *i.e.* expected ratios of aryl proton splittings are type (B) : type (I) : type (A) : : 1·34 : 2·37 : 4·98, *i.e. ca.* 1 : 2 : 4 as observed.





Molecular Orbital Model.—We can consider the delocalisation of the odd electron on to the aryl substituent as being similar to that in benzyl. Thus we look at the fragment consisting of the aryl group and the carbon atom to which it is attached. This problem, together with the variation of spin densities with the angle of twist about the carbon–aryl bond has already been discussed at various levels of sophistication.[3,4] However some understanding is to be gained using simple molecular orbital theory. If the dihedral angle is θ (see Figure 1) then we can resolve the

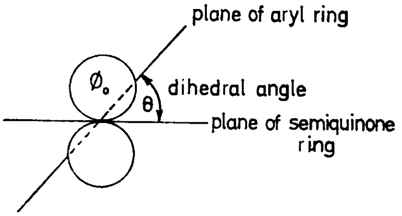


FIGURE 1

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[3] J. A. Pople and D. L. Beveridge, *J. Chem. Phys.*, 1968, **49**, 4725.

[4] W. J. Van den Moek, B. A. C. Rousseeuw, J. Smidt, W. G. B. Huysmans, and W. J. Mijs, *Chem. Phys. Letters*, 1972, **13**, 429.

2*p*- orbital of the adjacent carbon atom in the semiquinone ring into two parts, one, $\phi_0 \cos\theta$, which has the same symmetry as the π orbitals of the aryl substituent, and the other, $\phi_0 \sin\theta$, which has interactions only with the σ orbitals of the aryl group (see Figure 2). Spin density is therefore transmitted effectively *via* two distinct routes and we can write the hyperfine splittings as a simple sum of two terms [equation (1)].

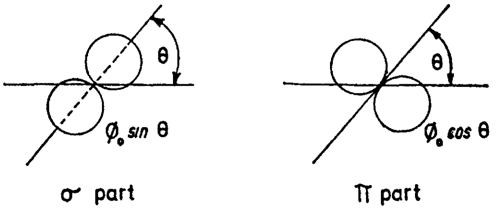

FIGURE 2

$$\begin{aligned} a(\theta) &= a_\pi(\theta) + a_\sigma(\theta) \\ &= a_\pi(0)\cos^{2}\theta + a_\sigma(90°)\sin^{2}\theta \qquad (1) \end{aligned}$$

We are interested in calculating the order of magnitude of the splittings and can estimate $a_\pi(0)$ and $a_\sigma(90°)$ either empirically, or theoretically using the parameters shown in Figure 3, which have been shown to account for a variety of coupling constants in n.m.r. spectra[5] and for certain effects in elimination reactions.[6] In both cases it is π interactions between bonds on adjacent atoms which are mainly responsible for the spin delocalisation. If we neglect differences in coulomb integrals the odd electron goes into a non-bonding orbital.

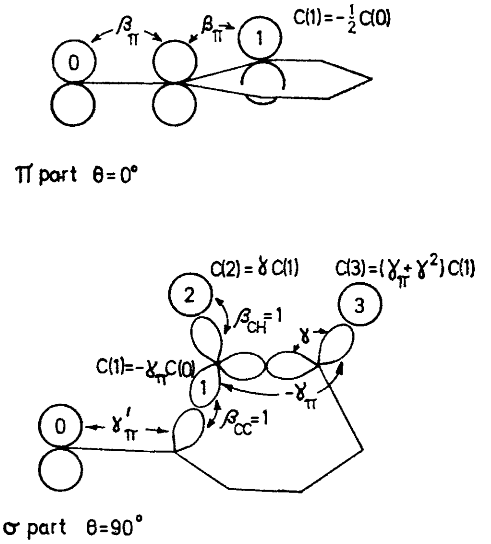

FIGURE 3 Some of the orbitals involved in extreme conformations, with the appropriate resonance integrals and coefficients

It has been found that values $\gamma_\pi \approx 1/4$, $\gamma \approx 1/4\sqrt{2}$, for the resonance integrals, roughly reproduce the coupling constants in vinyl and in phenyl (in the case of the *ortho*- and *meta*-protons). We use formula (2) for the splitting

$$a_{\mathrm{H}}(\sigma) = 508\rho_{\mathrm{H}} \qquad (2)$$

where ρ_{H} = spin density in the hydrogen 1*s* orbital.

This corresponds to an effective atomic number of hydrogen of unity. In the case of the π system we get the same formula as for benzyl [$a_{\mathrm{CH_2}} = 16{\cdot}5$, $a_o(\mathrm{H}) = 4{\cdot}9$, $a_m(\mathrm{H}) = 1{\cdot}5$, $a_p(\mathrm{H}) = 6{\cdot}1$ G], *i.e.* $a^\pi(\mathrm{H}) = -28\rho_{\mathrm{C}}$ where ρ_{C} = spin density in adjacent carbon p_π orbital. To be realistic we shall use the coupling constants in free benzyl to give us the π contribution and for the various kinds of proton we get the relationships (3)—(8) for the dependence on dihedral angle, for a given spin density ' ρ ' on the ' benzylic ' carbon.

for the π part:

$$\textit{ortho:}\ a_o^{\pi}(\mathrm{H}) = -8{\cdot}75\,\rho\cos^{2}\sigma \approx -a_o^{\pi}(\mathrm{CH_3}) \qquad (3)$$

$$\textit{meta:}\ a_m^{\pi}(\mathrm{H}) = +2{\cdot}6\,\rho\cos^{2}\theta \approx -a_m^{\pi}(\mathrm{CH_3}) \qquad (4)$$

$$\textit{para:}\ a_p^{\pi}(\mathrm{H}) = -10{\cdot}5\,\rho\cos^{2}\theta \approx -a_p^{\pi}(\mathrm{CH_3}) \qquad (5)$$

for the σ part:

$$a_o^{\sigma}(\mathrm{H}) = +0{\cdot}95\,\rho\sin^{2}\theta \approx +a_o^{\sigma}(\mathrm{CH_3}) \qquad (6)$$

$$a_m^{\sigma}(\mathrm{H}) = +2{\cdot}54\,\rho\sin^{2}\theta \qquad (7)$$

$$a_p^{\sigma}(\mathrm{H}) = 0 \approx a_m^{\sigma}(\mathrm{CH_3}) \approx a_p^{\sigma}(\mathrm{CH_3}) \qquad (8)$$

Only the value of ρ is different for the three types of radicals and to estimate it we use the coupling constants in the corresponding methyl substituted radicals[1] using $Q_{\mathrm{CH_3}} \approx 30$ G, *i.e.* from methylsemiquinone in primary (I) $a(\mathrm{CH_3}) = 2{\cdot}12$, in secondary ' (A) ', $a(\mathrm{CH_3}) = 5{\cdot}12$, and in secondary ' (B) ', $a(\mathrm{CH_3}) = 0{\cdot}95$ G.

For our purposes, changes in ' ρ ' with the substituent in the aryl ring are small, and for obtaining orders of magnitude, we can equate $a(\mathrm{H})$ with $a(\mathrm{CH_3})$. We shall go through with the calculation only for secondary radicals type ' (A) ', since these have the largest splittings.

The variation of proton splittings within the aryl group in the type (A) radicals is therefore given by equations (9)—(13). One might have expected the dihedral angle in

$$a_o(\mathrm{H}) = -1{\cdot}4\cos^{2}\theta + 0{\cdot}16\sin^{2}\theta \qquad (9)$$

$$a_o(\mathrm{CH_3}) = +1{\cdot}4\cos^{2}\theta + 0{\cdot}16\sin^{2}\theta \qquad (10)$$

$$a_m(\mathrm{H}) = 0{\cdot}44\cos^{2}\theta + 0{\cdot}42\sin^{2}\theta \qquad (11)$$

$$a_m(\mathrm{CH_3}) = -0{\cdot}44\cos^{2}\theta \qquad (12)$$

$$a_p(\mathrm{H}) = a_p(\mathrm{CH_3}) = -1{\cdot}75\cos^{2}\theta \qquad (13)$$

phenylsemiquinone to be of the order of 45°, that in the mono-*ortho*-substituted phenylsemiquinones to be 60° or more, and that in the 2,6-disubstituted phenylsemiquinones to be close to 90°. It is interesting therefore to compare the predicted couplings for these angles with those observed for the type (A) radicals when the aryl substituent is one of the methyl phenyl groups.

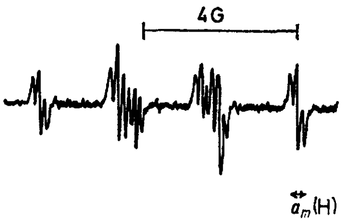

FIGURE 4 E.s.r. spectrum of the primary radical 2,6-dimethylphenylsemiquinone in 50% aqueous EtOH

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[5] W. T. Dixon, *J. Chem. Soc.* (*A*), 1967, 1879.

[6] W. T. Dixon, *Tetrahedron*, 1968, **24**, 5509.

DISCUSSION

From Table 3 we can see that the theory does account quite well for the variation of the various coupling constants, the most significant deviations from predicted behaviour being that of *o*-methyl proton coupling constants. This might have been expected since distortion is most likely to occur at the *ortho*-position [7] (bond bending of $C-CH_3$). From the theoretical point of view this simple approach gives much the same variations with dihedral angle as do more sophisticated theories. ' σ Spin delocalisation ', responsible for coupling constants when the angle is 90°, arises mainly from π type interactions involving the carbon hybrid orbitals each of which has 2/3 *p* character which can be resolved into part along the adjacent C–C bond and part perpendicular to it. In fact the π interactions between carbon sp^2 hybrid orbitals in ethylene are half the magnitude of the resonance integral assigned to the π bond, so they are by no means negligible.

TABLE 3

Comparison of calculated coupling constants of protons associated with aryl substituents with some of those observed for secondary radicals type (A) (in gauss)

	θ = 45°	Ar ≡ *p*-MeC_6H_4	Ar ≡ *m*-MeC_6H_4	θ = 60°	Ar ≡ *o*-MeC_6H_4	θ = 90°	Ar ≡ 2,6-$Me_2C_6H_3$	Ar ≡ 2,4,6-Me_3C_6H
a-(H)	(−) 0·62	0·58	0·52	(−) 0·23	0·28	(+) 0·16		
a-(CH_3)	(+) 0·78			(+) 0·47	0·11	(+) 0·16	0·09	0·08
a–(H)	(+) 0·43	0·31	0·32	(+) 0·42	0·28	(+) 0·42	0·31	0·32
a–(CH_3)	(−) 0·22		0·16	(−) 0·11		0		
a-(H)	(−) 0·87		0·52	(−) 0·45	0·28	0	0	
a-(CH_3)	(+) 0·87	0·58		(+) 0·45		0		0

meta-*Proton Splittings*.—Out of the theory and also from the results comes the fact that the *meta*-proton splittings are remarkably constant throughout the various series of aryl substituents studied. This has also been observed in aryl nitroxide radicals.[8] This proves that the coupling constant must have the same *sign* at all dihedral angles. Since in the near perpendicular conformations these splittings arise effectively from hyperconjugation, *i.e.* direct transmission of spin density, the sign should be *positive*. This means that if we accept the spin polarisation mechanism in π type radicals we are led to confirm empirically that the spin density in the *meta*-carbon $2p_\pi$ orbital must be *negative*.

Dihedral Angles.—The disappearance of hyperfine splitting due to *ortho*- or *para*-protons or methyl protons, in the primary and secondary type (B) radicals, together with appropriately low values in the secondary type (A) radicals, confirms that when there is a 2,6-disubstituted aryl ring, the dihedral angle between the two rings is close to 90°. Similarly when there is no *ortho*-substituent on the aryl ring, the angle, by comparison with theory, is apparently of the order of 45°. With a single *ortho*-substituent the situation is intermediate between these two.

Substituent Effects.—When substituents are in the *para*-position, quite definite effects are observed in the coupling constants of protons attached to the original semiquinone ring. When the same substituents are in either the *ortho*- or in the *meta*-positions of the aryl ring, they have very little effect on the spin densities around the semiquinone ring. This is because, in the latter case, there is insufficient conjugation and in the former, presumably, there is less conjugation due to an increased dihedral angle. The most obvious case is that when the substituent on the aryl group is hydroxy (see Table 1) but other cases (*e.g.* NO_2) show similar relationships. The direction of effects induced by substituents on the aryl ring have been discussed already but what is important in the light of the present evidence is that the effects of a given substituent must be largely determined by the relative configuration of the π electron system, *i.e.* the effects of substituents are transmitted *only by the π electron system*. This point is usually assumed but seldom proved so directly. The reason why transmission of polar effects or of spin density is inefficient in the σ framework is because the σ bonds are so strong that they effectively damp out the effects of different polar groups.

^{19}F *Splittings*.—Two points stand out here; first the ^{19}F splitting in the *o*-fluoro-derivative is unexpectedly large, compared with either the *p*-fluoro case, or with the *o*-proton splitting which in other systems is usually about half the corresponding ^{19}F coupling constant. Secondly, the coupling of a *m*-fluorine nucleus could only be resolved in the secondary type (A) radical spectrum. Both of these points can be explained by the fact that when fluorine is attached to a π system, the ^{19}F coupling constants are thought to be of opposite sign to corresponding proton splittings [9] and has been proved in some cases, *e.g.* by n.m.r. contact shifts in stable nitroxide radicals.[10] This is so because spin density can get directly onto the fluorine atom *via* the $F(2p_\pi)$ orbital. Similarly in the case of β-fluorine coupling [10,11] spin density is transmitted onto a $F(2p_\sigma)$ orbital, presumably also giving rise to a *positive* contribution to the hyperfine splitting. The result of these two effects is that $a_\pi(^{19}F)$ and $a_\sigma(^{19}F)$ have the same sign

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for *o*-fluorine but have opposite signs in the case of *m*-fluorine nuclei, because in the π part there is negative spin density derived from the *m*-carbon $2p_\pi$ orbital. From our calculations above a_π^m and a_σ^m are approximately equal for hydrogen nuclei and of the same sign, *i.e.* for an angle of *ca.* 45°. For fluorine nuclei in the *meta*-position these two contributions would be expected also to have the same magnitude (*i.e.* about twice the proton splittings) but of opposite sign, so they cancel so effectively that the resultant splitting can be resolved only in the spectrum from the secondary radical type (A).

For *o*-fluorine, the two contributions are both positive and add to each other giving a comparatively large coupling constant.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E4 instrument. To obtain the primary radicals a solution of the arylhydroquinone (0·01M) in ethanol was mixed with an equal volume of 1% sodium hydroxide solution, both flow and static methods being used. The secondary radicals were obtained by adding an aqueous solution of the hydroquinone (0·05M) to an equal volume of 15% sodium hydroxide. A mixture of the two secondary radicals was initially obtained, but on leaving the solutions the spectra from the type (B) radical decayed leaving a pure spectrum from type (A). Since the overlap of the spectra from (A) and (B) was, at the most, very small, both could be analysed.

Materials.—The arylquinones, some of which were new compounds, were obtained by direct arylation of *p*-benzoquinone via the diazonium salts according to the method of Brassard and L'Écuyer.[12]

The extra steric strain in the *ortho*-substituted arylquinones lowered the m.p. in these compounds and they were initially produced as oils. They were obtained pure by repeated crystallization from light petroleum (at *ca.* −50 °C) until their m.p.s were sharp and the e.s.r. spectra did not reveal impurities.

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