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SYMMETRICAL DISTRIBUTION OF SPIN DENSITY IN NEUTRAL ARYLOXY RADICALS DERIVED FROM 2,2'-DIHYDROXYBIPHENYLS

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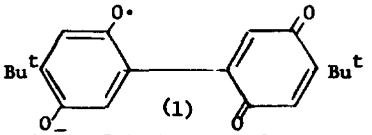
We have found that strong e.s.r. signals are obtained when degassed solutions of suitably substituted 2,2'-dihydroxybiphenyls are allowed to mix with silver oxide in another arm of an evacuated sample tube. The radicals are of sufficient stability to be examined in this stationary system at temperatures ranging from -50 to +25°, and no secondary radicals were observed. Selective deuteration of the ring protons with deuterium chloride[1] and of the hydroxyl protons with deuterium oxide has allowed us to assign unequivocally the hyperfine splitting constants shown in the Table. These were confirmed by computer simulation of the spectra. The small size of the splitting constants suggests that much of the unpaired electron density is associated with the 2,2' oxygen atoms. Splittings by hydrogens at the 4,4', 6 and 6' positions and by the t-butyl hydrogens were too small to be resolved.

In each case a doublet splitting by the remaining phenolic hydroxyl hydrogen was observed and, significantly, pairs of equivalently situated hydrogens on each ring gave rise to the same splitting, showing that the unpaired electron was shared equally by the two rings.

As no evidence of alternating line width was observed within the temperature range used, unlike the situation encountered with protonated *o*-benzosemiquinone[2], we suggest that the equivalence of the rings is established by a very rapid intramolecular process in which the hydroxyl hydrogen is alternately bonded to each oxygen. This can be achieved with consummate ease in this particular system by adjustment of the dihedral angle between the rings.

It is significant that radical *anions* of 2,2'-dihydroxybiphenyls do not show a sharing of unpaired spin between the rings. Only in the mono-anion radicals of diquinones such as (1), where intramolecular electron transfer to the quinonoid ring is facile, and where more opportunities for delocalisation exist, do the rings again become equivalent[3].



(1)

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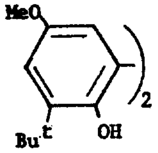
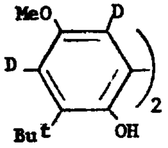
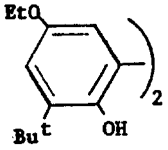
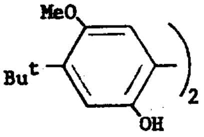
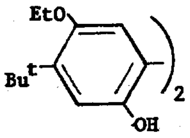
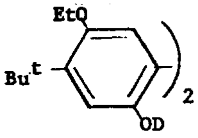
TABLE

Hydrogen hyperfine splitting constants, in gauss, multiplicities in parentheses, and g-values for radicals.

Phenol	a_{-OH}	$a_{-3,3'H}$	$a_{-O-alkyl}$	g-value
	0.50(2)		0.83(7)	2.0043
	0.50(2)		0.83(7)	
	0.50(2)		0.92(5)	2.0042
	0.50(2)	1.38(3)	0.90(7)	2.0042
	0.49(2)	1.38(3)	1.18(5)	2.0042
		1.50(3)	1.01(5)	

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(2) I.C.P. Smith and A. Carrington, Mol. Phys., 1967, 12, 439.
(3) F.R. Hewgill and L.R. Mullings, Aust. J. Chem., 1975, 28, 355.