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LONG-RANGE SPLITTINGS IN THE E.S.R. SPECTRA OF POLYCYCLIC SEMIQUINONES

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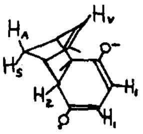
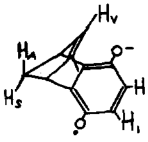
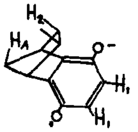
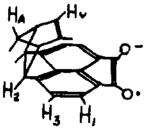
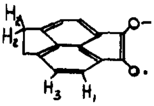
Recently several examples of large ESR splitting constants for hydrogens on carbons β to carbons bearing formal spin density have been reported for semidione radical anions.[1,2] These examples demonstrate that large splitting constants are observed when the $H\text{-}C_\beta\text{-}C_\alpha\text{-}C\cdot\text{-}p_z$. grouping is in the W-plan, allowing back-lobe overlap of the $H\text{-}C_\beta$ sp^3 orbital with p_z. The only example reported of a γ-hydrogen splitting, where that hydrogen is not a $C_\beta\text{-}C_\gamma$ double bond (allowing $p_z\text{-}p_z$ overlap to introduce spin to the pi system) is that of 6,6-dimethyl[3.1.1]-bicycloheptane-2,3-semidione. Russell and coworkers[1] observed a splitting of 0.426 for one of the methyl groups. We here report additional examples of γ-hydrogen couplings, together with comments on coupling mechanisms.

Samples of I and IV (Table I) were prepared for ESR study[3] by *in situ* electrolytic reduction of the diones in .05 *M* tetrabutylammonium perchlorate-DMSO. II and III were prepared by basic air oxidation of the hydroquinones[4] in .1 M KOtBu-DMSO. I easily aromatizes to II (spectrum

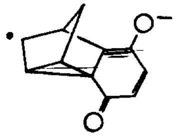
TABLE I

Radical	a_H	Assignment
 I	5.71 (2H)	H_1[a]
	4.31 (2H)	H_2[a]
	0.21 (3H)	H_V, H_A
 II[2]	2.35 (2H)	H_1
	0.80 (1H)	H_A
	0.40 (3H)	H_V, H_S
 III	2.55 (2H)	H_1
	0.66 (3H)	H_2, H_A
 IV	1.07 (4H)	H_1, H_2
	0.21 (3H)	H_3, H_A
 V[5]	1.15 (2H)	H_1
	1.38 (4H)	H_2
	0.21 (2H)	H_3

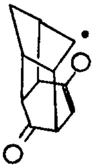
(a) These assignments were made from HMO calculations on 2,3-dihydrobenzoquinone, which give (for Q = 24) 5.67 G for H_1, and 4.98 G for H_2.[6] The expected value for H_2 of I is somewhat lower because of the inductive effect of the two carbon substituents.

identical to that published[2]), but was stable enough under our conditions to record spectra. The dione leading to IV was prepared by addition of cyclopentadiene to pyracyloquinone,[7a] and shown to be endo by NMR.[7b]

Since II has been shown not to give observable bridgehead splittings,[2] I and IV are not expected to have these splittings either; the C-H bond angles in these cases are even less favorable for splitting. Furthermore, IV only shows one proton splitting in addition to the aromatic ring protons. Thus I has a vinyl splitting of 0.21 G, II 0.40 G, and IV unobservable (V is a good model for the ring protons of IV and thus two of the 0.21 G split protons must be H_3). Kosman and Stock have proposed overlap of the sort shown in resonance structure VI to account for the vinyl spin in II. We propose a similar p_v-p_z. overlap, structure VII, to account for this phenomenon in I. That C_1 and C_V can become close enough for overlap of their p-orbitals is demonstrated by the photochemical ring closure involving these centers.[8]



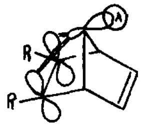
VI



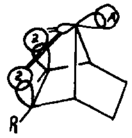
VII

The overlap shown in VII is virtually impossible for IV, which is consistent with H_V being too small to observe.

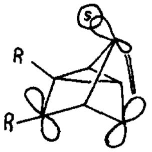
Although II gives appreciable H_A and H_S splittings, the spectra of I, III, and IV show splitting by only one of the protons.[9] For the large H_A splittings in II and III,



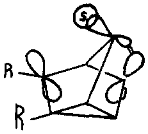
VIII



IX



Xa



Xb

overlap of the type shown in structure VIII has been generally accepted.[1,2] We propose a similar type of overlap for I and IV, involving the back lobe of the bond to H_A and the H_2 orbitals (see structure IX) instead of p-orbitals, to account for the large H_A splittings. But II, and only II of this series, shows a high H_S splitting. A reasonable interpretation of this splitting involves the back lobe overlap depicted in structures Xa and Xb. The lack of unsaturation in III and of observable spin density at these vinyl positions of IV, both of which show no H_S splitting, is consistent with this proposal. The lower spin density at the vinyl positions of I predicts a smaller H_S splitting than in II. Furthermore, models of VII indicate a much poorer geometry for overlap than for VI (overlap shown in Xa and b). These observations are consistent with the data.[10]

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9. See Ref. 1 for other examples of large differences in H_S and H_A splitting in similar systems.
10. We wish to acknowledge partial support from the Wisconsin Alumni Research Foundation (SFN) and the National Institutes of Health, GM 13598-01 (BMT).