Condensation of bromoethane-2,2,2-d_3 (5.6 g, 0.05 mol) with diethyl malonate, followed by hydrolysis and decarboxylation,[27] gave 2.49 g (55%) of butanoic acid-4,4,4-d_3.

Treatment of the acid with thionyl chloride resulted in the formation of butyryl chloride-4,4,4-d_3; a benzene solution of the crude acid chloride was added to a solution containing an equivalent amount of dipentylcadmium.[28] The desired ketone, 4-nonanone-1,1,1-d_3 (97% d_3), was isolated in high yield and purified further by repeated vapor phase chromatography on a 10-ft Carbowax 20M column operated at 170°.

4-Nonanone-7,7-d_2 (IV). Propionic acid was reduced with lithium aluminum deuteride in dry diglyme.[25] The resulting propanol-1,1-d_2 was converted to the corresponding bromide by the procedure of Wiley, *et al.*,[26] and homologated by condensation with diethyl malonate, followed by hydrolysis and decarboxylation.[24] The resulting pentanoic acid-3,3-d_2 was converted to 1-bromopentane-3,3-d_2 by the usual procedures.[25,28]

Conversion of the bromide to the corresponding organocadmium reagent, followed by treatment with an equivalent amount of butyryl chloride, gave 4-nonanone-7,7-d_2. Purification was accomplished by vapor phase chromatography. The resulting ketone was of 98% d_2 isotopic purity.

4-Nonanone-3,3,5,5-d_4 was prepared by the repeated equilibration of the parent ketone with deuteriomethanol containing 10% heavy water and a catalytic amount of sodium deuterioxide. The product was recovered by removing the solvent under vacuum. The discolored liquid was further purified by vapor phase chromatography through a 10-ft Carbowax column (170°) preequilibrated with heavy water.[29] The resulting d_4-ketone was 94% pure.

1-Methylcyclobutanol and 1-Methylcyclobutanol-1′,1′,1′-d_3. The preparation of these compounds has already been described.[11,30]

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(27) R. Adams and R. M. Kamm, "Organic Syntheses," Coll. Vol. I, Wiley, New York, N. Y., 1932, p 250; E. B. Vliet, C. S. Marvel, and C. M. Hseuh, "Organic Syntheses," Coll. Vol. II, Wiley, New York, N. Y., 1943, p 416.

(28) J. Cason and F. S. Prout, "Organic Syntheses," Coll. Vol. III, Wiley, New York, N. Y., 1955, p 601.

(29) M. Senn, W. J. Richter, and A. L. Burlingame, *J. Amer. Chem. Soc.*, **87**, 680 (1965); W. J. Richter, M. Senn, and A. L. Burlingame, *Tetrahedron Lett.*, 1235 (1965).

(30) D. A. Semenow, E. F. Cox, and J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 3221 (1956).

Heterocyclic Radical Ions. IV. Electron Spin Resonance Spectra of Conformationally Mobile Semifuraquinones[1]

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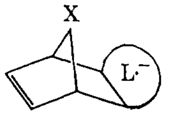
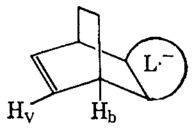
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received January 22, 1970*

Abstract: The esr spectra of anions of dimethylmaleic anhydride, tetrahydrophthalic anhydride, 3,6-dihydrophthalic anhydride, and three methylated derivatives are reported and discussed. The methyl and vinyl splittings of 4-methyl-3,6-dihydrophthalic anhydride were about the same size, but it was concluded that the methyl splitting was not arising solely from π spin density in the 4,5-vinyl π system.

The mechanisms involved in spin delocalization to protons γ to spin-bearing p orbitals have been a subject of considerable discussion in recent years, especially since the discovery by the groups of Russell[3] and Stock[4] that the esr splitting constants of such γ protons are considerably enhanced in rigid, strained systems. One case of interest has been the interaction of a homoconjugated vinyl group with a spin-bearing π system, as that generalized in structure **1** below.[5]



1



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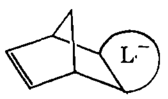
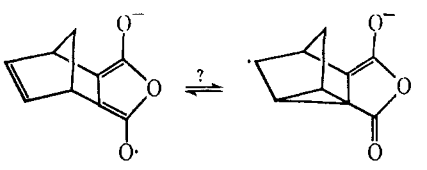


3

The vinyl splitting is considerably enhanced when a bridging X group is present in the cyclohexadienyl system, but larger splittings are observed for X = CH_2–CH_2 (**2a** and **2b**) than when X = CH_2 (**3a** and **3b**) in semiquinones and semifuraquinones. Since the C_2–C_6 distance should be larger for **2** than for **3**, we have argued[1] that this is evidence against a mechanism in which spin is transmitted by simple physical overlap of the label and vinyl π systems. Furthermore, the vinyl splitting of **2c** is only 37% as large as that of **2a**, although the α spin density of semidiones is greater than that of semifuraquinones. One possibility which has been considered[1-3] for the spin delocalization has been a homoallylic interaction of the sort depicted in Ia–b. If such delocalization or tautomerism were



Ia Ib

important, the vinyl splitting would arise from π spin density being introduced into the vinyl π system. If this were the case, replacing a vinyl hydrogen by a methyl group should result in a methyl splitting about the same size as the vinyl splitting. Russell's group[3] investigated a substituted 5,6-dimethyl **2c**, which had a methyl splitting slightly larger than the vinyl splitting of **2c** itself (0.49 *vs.* 0.41 G); they interpreted this in

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(1) For Part III see S. F. Nelsen and E. D. Seppanen, *J. Amer. Chem. Soc.*, **89**, 5740 (1967).

(2) Alfred P. Sloan Fellow, 1968–1970.

(3) G. A. Russell, G. W. Holland, and K. Y. Chang, *J. Amer. Chem. Soc.*, **89**, 6629 (1967), and references therein.

(4) D. Kosman and L. M. Stock, *ibid.*, **91**, 2011 (1969), and references therein.

(5) $F\cdot^-$ is used to symbolize the $[(=C—CO)_2O]\cdot^-$ "spin label" common to many of the compounds discussed. The suffix a will be used for semifuraquinones, b for semiquinones, and c for semidiones.

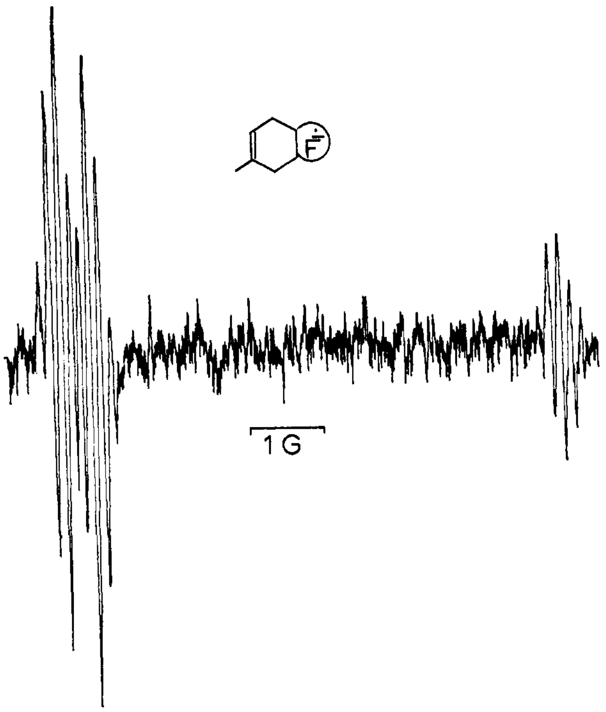


Figure 1. The two major high-field lines of **8a**, illustrating the narrow quintet caused by $a(CH_3) \simeq a(H_v)$, and the doublet of quintets caused the two different two-hydrogen β splittings. A decrease in intensity, caused by radical decomposition during the scan, is obvious.

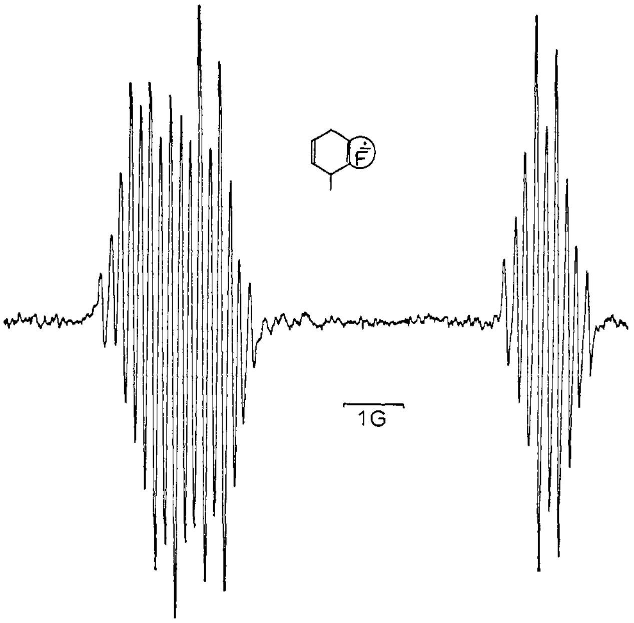


Figure 2. The upfield half of the spectrum of **6a**. The nine-line pattern for the outer line is a result of $a(CH_3)$ being only slightly different from half of the two vinyl hydrogen splittings. The inner line consists of three such patterns partially overlapping, since the three β hydrogen splittings are slightly different.

terms of the homoallylic interaction of the type **1a–b**. Kosman and Stock, however, observe no methyl splitting for 5-methyl-7-isopropyl **2b** and 3,5-dimethyl **3b** (X = CH_2), and therefore rejected the homoallylic interaction as being important for semiquinones, instead preferring a spin polarization mechanism in which spin density reaches the vinyl protons without transferring significant spin density to the vinyl π system.

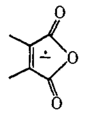
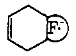
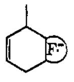
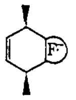
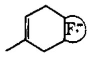
We have chosen a slightly different approach to the problem of homoallylic interaction, and have investigated several 3,6-dihydrophthalic anhydride anions. These have the disadvantage that the vinyl splittings are quite small, but do have an additional probe for spin density distribution in the β-hydrogen splitting.

Results

The structures and splittings observed for the semifuraquinone studies are summarized in Table I.

The large splittings of **4a**–**9a** were all consistent with the number of β protons; **4a** showed a septet, **5a**, **8a**, and **9a** quintets, **6a** a quartet, and **7a** a triplet, under conditions of low resolution. At higher resolution, however, the unsymmetrical radicals **6a** and **8a** clearly had unequal β splittings. The outer lines of **8a** consisted of quintets (Figure 1), but major lines 2 and 4 were each a doublet of quintets, and the center line a 1:2:1 triplet of quintets, consistent with two pairs of large β splittings, the small methyl and vinyl splittings being approximately (±0.05 G) the same. The spectrum of **6a** was even more complicated, for here the outer lines were nine-line patterns, and lines 2 and 4 clearly showed three different one-proton β splittings were present (Figure 2). In **7a** we were unable to observe a difference between twice the vinyl splitting and the six-proton methyl splitting. At room temperature **9a** was not quite at the high-temperature limit, since the intensities observed were much closer to 1:2:4:2:1 than 1:4:6:4:1.

Table I. Esr Splitting Constants (G) for Some Conformationally Mobile Semifuraquinones

Radical anion	No.	a_β (no. of H)	a_v (no. of H)	a_{other} (no. of H)
	**4a**	6.10 (6)		
	**5a**	6.35 (4)	0.19 (2)	
	**6a**	5.75 (1), 6.65 (1) 7.00 (1)	0.20 (2)	0.33 (3)
	**7a**	5.83 (2)	*Ca.* 0.15 (2)	*Ca.* 0.30 (6)
	**8a**	6.40 (2), 6.79 (2)	*Ca.* 0.15 (1)	*Ca.* 0.15 (3)
	**9a**	7.63 (4, av)		Unobserved

Discussion

Since we observed a methyl splitting for **8a** of about the same size as the vinyl splittings in these systems, this result alone seems to favor the view that the vinyl splitting arises largely from π spin density being introduced into the vinyl group, as stated above. Replacing hydrogens β to a spin-bearing p orbital by methyl certainly does decrease the observed splitting markedly; the methyl splittings of **6a** and **7a** are less than one-tenth the size of the β-hydrogen splitting of **5a**. The same is true for replacing aliphatic γ protons by methyl, as at the 7-*anti* position of **3c**, which lowers the splitting from 6.54 to 0.53 G.[6] Thus, the size of the methyl splitting of **8a** is surprisingly large, and in direct contrast to Kosman and Stock's result[4] for the methylated **1b** and **3b** system.

If there actually is significant vinyl spin density in **5a**–**8a** introduced by a homoallylic interaction such as that shown in **4a**–**4b**, the signs of the coefficients at positions 1 and 4 should be opposite to those at 2 and 5 (for the semifuraquinone—for semidiones all the signs should be the same). If this were the case, the β splittings must be lowered substantially; as Whiffen first pointed out,[7] for a methylene interacting with two π systems, $\rho_{C_\alpha}{}^{\pi}(=(c_{C_\alpha}{}^{\pi})^2)$ in the usual McConnell equation for a_β must be replaced by $(ca^\pi + cb^\pi)^2$, where ca^π and cb^π are the coefficients at the adjacent sp^2-hybridized carbons. This is experimentally verified by comparison of the methylene splitting for cyclohexadienyl radical[8] (47.6 G, $ca = cb$) with that for cycloheptatrienyl anion[9] (2.16 G, $ca^\pi = -cb^\pi$) or with cyclobutenyl radical[10] (4.45 G, $ca^\pi = -cb^\pi$). In the latter two cases the hyperconjugative contribution to the methylene splitting is cancelled leaving presumably only the considerably smaller spin polarization contribution.

Thus to the extent that there is π spin density in the vinyl group of **5a**, the methylene splittings should be lowered. Unfortunately direct calculation of the size of the β splitting of **5a** without any vinyl π spin density is not possible. We have instead chosen to use **9a** as a model for this splitting. The size of β splittings is obviously very dependent on geometry, and the equation $a_\beta = (A + B\cos^2\theta)\rho_{C_\alpha}{}^{\pi}$, where θ is the C$_\beta$–H p-orbital axis dihedral angle, is generally accepted.[11] Application of this equation leads to a prediction that a_β for **9** should be about 1.5 times that for **4**. Enhancements this large are not observed experimentally, however, and a_β for **9a** is only 1.25 times that for **5a**, while a_β of **9c** is 1.41 times that of **5c**. There could be a number of reasons for such deviations, including an inherently lower β value for methylene hydrogen than for methyl, a value for $\langle\theta\rangle$ significantly different from 120°, and inexactness in the $\cos^2\theta$ relationship. Using the experimental methylene splitting for **9a**, and accepting nearly identical H–C$_\beta$–H angles and the same effective B value for **9a** and **5a**, an estimate of how much vinyl π spin density would give the observed a_β for **5a** can be made; by using **4a** to obtain $\rho_\alpha{}^{\beta} \simeq 0.22$ the effective value for Q_β of **9a** is about 22.9, which gives the result that a $\rho_v{}^{\pi}$ of only 0.8% that of $\rho_\alpha{}^{\pi}$ would give rise to the decrease in methylene splitting observed. From the size of the **5a** vinyl splitting, a $\rho_v{}^{\pi}$ of about 0.008 would be required if the vinyl splitting were to arise completely from vinyl π spin density, and a methylene splitting of about 5.0 G would have been expected. This sort of estimation of expected splitting is obviously quite crude, but the size of the β splitting for **5a** does not support the notion that most of the vinyl splitting arises from vinyl π spin density. If the effective B value for the doubly allylic β hydrogens of **5** were substantially larger than for those of **9**, more vinyl spin density could be accommodated.

The conclusion of this work is that vinyl methyl substitution and β splittings give apparently conflicting answers in the **5** system, and that caution should be used in interpreting vinyl methyl splittings in other systems as indicating substantial π spin density.

Experimental Section

The dialkylmaleic anhydrides employed were prepared by literature methods, and purified by sublimation. Melting point and nmr data for the compounds used appear in Table II. Esr measurements were performed on a Varian E-3 spectrometer, using reduction in 0.05 M tetrabutylammonium perchlorate in DMSO inside the cavity. The splittings were all measured on the same day, and calibrated with quinone as standard. The 6.56-G measurement for the a_β of **5a** previously reported[1] was run on a separate instrument, and we believe the value reported here to be more accurate.

Table II. Melting Point and Nmr Data for Dialkylmaleic Anhydrides

Compd no.	Mp, °C (lit. mp)	Nmr (δ, CDCl$_3$)
4	95–95.5 (95–96)[a]	2.09 (s)
5	148–149.5 (145–146)[b]	5.90 (m, 2 H); 3.12 (m, 4 H)
6	60–61 (61–62)[b]	5.75 (m, 2 H); 3.13 (complex, 3 H), 1.36 (d, J = 6.5, 3 H)
7	80–81 (80–80.5)[c]	5.67 (d, J = 1.3, 2 H); 3.25 (m, 2 H); 1.35 (d, J = 7, 6 H).
8	100–101 (101–102)[b]	5.57 (7 lines, 1.5 Hz sepn, 1 H); 2.05 (br s, 1 H). 1.85 (br s, 3 H)

[a] E. Ott, *Chem. Ber.*, **61**, 2131 (1928). [b] U. K. Kucherov and Ya. Grigor'eva, *J. Gen. Chem. USSR*, **31**, 408 (1961). [c] U. F. Jucherov and I. I. Zemskova, *ibid.*, **31**, 416 (1961).

Acknowledgment. We wish to thank John Gillespie for the preparation of **4**, and Professor Leon Stock for helpful discussions. This work was financially supported by the National Science Foundation, The Research Corporation, and the Wisconsin Alumni Research foundation.

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[6] G. A. Russell and K. Y. Chang, *J. Amer. Chem. Soc.*, 87, 4381 (1965).

[7] D. H. Whiffen, *Mol. Phys.*, 6, 233 (1963).

[8] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 39, 2147 (1963).

[9] D. H. Levy and R. J. Meyers, *ibid.*, 43, 3063 (1965).

[10] P. J. Krusic, J. P. Jesson, and J. H. Kochi, *J. Amer. Chem. Soc.*, 91, 4566 (1969).

[11] See ref 4 for a discussion.