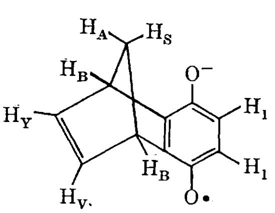
Long-range Coupling in Bicyclic Molecules

By DANIEL KOSMAN and LEON M. STOCK*

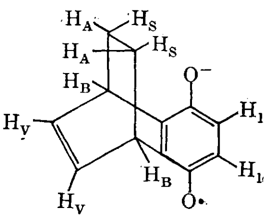
(*Department of Chemistry, University of Chicago, Chicago, Illinois,* 60637)

THE coupling mechanism for vinyl hydrogen atoms has been discussed in recent reports concerning the spin density distribution in unsaturated bicyclic semiquinones,[1-3] such as (I) and (II), semidiones,[4] and semifuraquinones.[5] Four rather distinct coupling mechanisms require consideration. A most reasonable interpretation is that electron density is delocalized *via* an important bonding interaction between C-2 and C-6 as illustrated in the valence bond structures.[1-4]



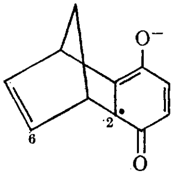
(I)

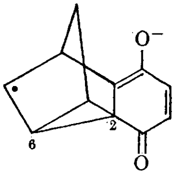
a_H = 2·36 gauss (2H); H_1
a_H = 0·80 gauss (1H); H_A
a_H = 0·40 gauss (3H); H_V,H_S



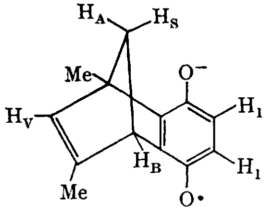
(II)

a_H = 2·72 gauss (2H); H_1
a_H = 0·54 gauss (4H); H_V,H_A
a_H = 0·13 gauss (2H); H_S



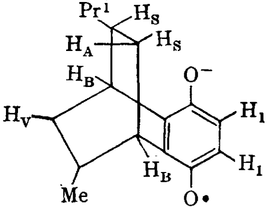


An equally satisfactory interpretation is that these structures illustrate an equilibrium rather than a delocalization.[5] There is ample precedent for an equilibrium of this kind in the free-radical chemistry of norbornadienes.[6] Electron density may also be transferred by rapid electron exchange between isolated quinone and ethylenic π-orbitals.[7] A fourth possibility, suggested by the importance of w-plan arrangements in the coupling of hydrogen nuclei in bicyclic molecules, is spin polarization. Barfield has proposed an elegant model based on this concept for such long-range nuclear couplings.[8] Barfield's theory considers both indirect (through bond) and direct coupling. The important inference of the first three interpretations is that spin density is detected at the vinyl hydrogen atoms because electron density is introduced into the ethylenic π-orbitals. The fourth suggestion does not require the transfer of electron density. This interpretation requires only that the electrons in the vinyl carbon–hydrogen bond are spin polarized by an interaction with the spin density in the quinone nucleus. To test this point, we examined the spectra of semiquinones (III) and (IV). Semiquinone (III) was prepared by the base-catalysed air oxidation of the hydroquinone which was generated from the corresponding diacetate. Semiquinone (IV) was prepared directly from the adduct[10] of benzoquinone and 2-methyl-5-isopropylcyclohexa-1,3-diene in the same manner. The spectroscopic assignments based on the results for other closely related radicals[1,2] are shown:



(III)

a_H = 2·51 gauss (1H); H_1
a_H = 2·18 gauss (1H); H_1
a_H = 0·81 gauss (1H); H_A
a_H = 0·54 gauss (1H); H_V
a_H = 0·34 gauss (1H); H_S
a_{Me} ⩽ 0·05 gauss



(IV)

a_H = 2·55 gauss (2H); H_1
a_H = 0·47 gauss (1H); H_A
a_H = 0·47 gauss (1H); H_V
a_{Me} ⩽ 0·05 gauss

The first three proposals predict that the coupling constant for the vinyl methyl group, a_{Me}, and for the vinyl hydrogen atom, a_H, should be very similar inasmuch as they are both largely determined by the electron density, ρ_c^π, in the adjacent carbon π-orbital.[9,11,12] According to the well known relationships,[9,11,12] the ratio for these constants is

$$\frac{a_{Me}}{a_H} = \frac{\rho_c^\pi B \cos^2\theta}{\rho_c^\pi Q} \simeq -1$$

when B is 50 gauss, $\cos^2\theta$ is 0·5, and Q is -25 gauss. The experimental results reveal, in contrast to this prediction, that the ratio is very small. The very similar values of a_H for the remaining hydrogen atoms of these methylated compounds and the unsubstituted derivatives reveal that the methyl group does not seriously perturb the distribution of spin density. The fact that a_{Me} is small therefore indicates that electron density is not transferred to the ethylenic π-bond. Accordingly, a coupling mechanism not involving the transfer of electron density is required by these new data. Either indirect (through bond) or direct spin polarization of the electrons of the vinyl carbon–hydrogen bond would accommodate these results.

(*Received, March 18th*, 1968; *Com.* 329.)

[1] D. Kosman and L. M. Stock, *J. Amer. Chem. Soc.*, 1966, **88**, 843.

[2] D. Kosman and L. M. Stock, *Tetrahedron Letters*, 1967, 1511.

[3] S. F. Nelson and B. M. Trost, *Tetrahedron Letters*, 1966, 5737.

[4] G. A. Russell, G. W. Holland, and Kuo-Yuan Chang, *J. Amer. Chem. Soc.*, 1967, **89**, 6629.

[5] S. F. Nelson and E. D. Seppanen, *J. Amer. Chem. Soc.*, 1967, **89**, 5740.

[6] C. R. Warner, R. I. Strunk, and H. G. Kuivila, *J. Org. Chem.*, 1966, **31**, 3381 and references therein.

[7] H. M. McConnell, *J. Chem. Phys.*, 1961, **35**, 508.

[8] M. Barfield, *J. Chem. Phys.*, 1964, **41**, 3825.

[9] H. M. McConnell and D. B. Chestnut, *J. Chem. Phys.*, 1958, **28**, 107.

[10] O. Diels and K. Alder, *Ber.*, 1929, **62**, 2337.

[11] A. D. McLachlan, *Mol. Phys.*, 1958, **1**, 234.

[12] M. C. R. Symons, *J. Chem. Soc.*, 1959, 277.