Tetrahedron Letters No.16, pp. 1511-1515, 1967. Pergamon Press Ltd. Printed in Great Britain.

The EPR Spectra of Semiquinones. Part IV Long Range Coupling Constants in Bicyclic and Tricyclic Derivatives.

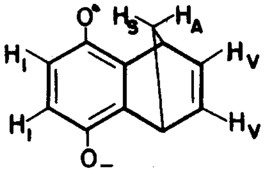
Daniel Kosman and Leon M. Stock

Department of Chemistry, University of Chicago

Chicago, Illinois 60637

(Received 3 January 1967)

The EPR spectra of several unsaturated bicyclic semidiones and semiquinones were recently reported.[1-3] The study of group labeled derivatives of **Ia** revealed that the vinyl protons and both the *syn* and *anti* protons were coupled.[2-4]



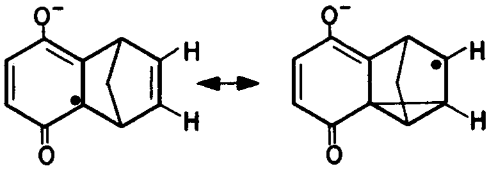
a_H = 2.36 gauss (2H); H_1

a_H = 0.80 gauss (1H); H_A

a_H = 0.40 gauss (3H); H_S, H_V

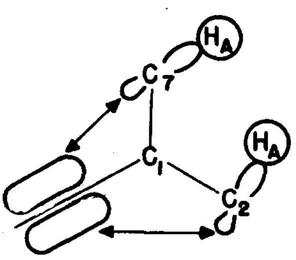
Ia

The spin density at the vinyl protons may be related to the importance of valence bond contributions, II and III. The spin density at the *anti* proton may be related to the W-plan arrangement of the *anti* proton and the aromatic ring, **IV**.[1-3]

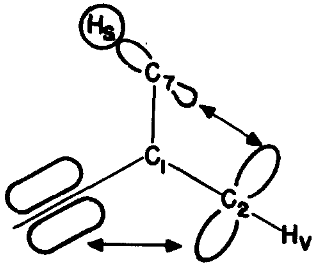


II **III**

The origin of the coupling of the *syn* proton is less certain. Recently, Nelsen and Trost[3] proposed that the spin density at the *syn* proton resulted from the rearside overlap of the carbon-hydrogen *sp^3* orbital with the *pi* bond, **V**.



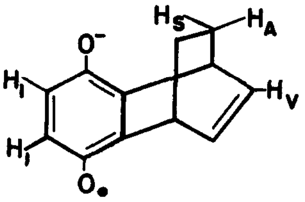
IV



V

New results are presented in this communication that strongly support this interpretation and that also suggest the importance of long range couplings through *pi* bond-*pi* bond interactions.

The investigation was first extended to the study of semiquinones **VIa** and **VIIa**.[5] The coupling constants and their assignments are summarized below each structure.

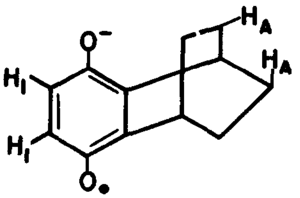


VIa

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



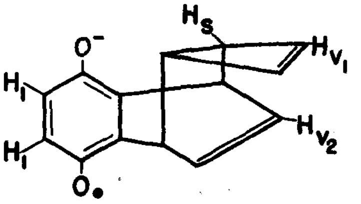
VIIa

a_H = 2.78 gauss (2H); H_1

a_H = 0.45 gauss (4H); H_A

The assignments for VIa and VIIa are based on the fact that the a_H values for vinyl and *anti* protons are usually somewhat larger than a_H for *syn* protons.[1-3] One striking feature is the coupling of the *syn* protons in VIa but the absence of this coupling in VIIa. This finding is, of course, consistent with the suggestion[3] that the coupling mechanism involves the *pi* bond.

To verify these assignments we prepared hydroquinones VIII and IX and both were hydrogenated to X.[5] The spectroscopic results are summarized below the structures.

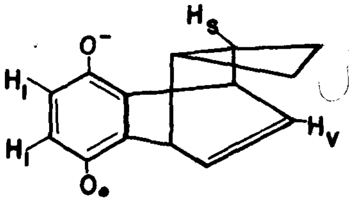


VIIIa

a_H = 2.65 gauss (2H); H_1

a_H = 0.44 gauss (2H); H_{V_1}

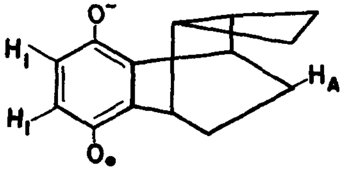
a_H = 0.14 gauss (4H); H_S, H_{V_2}



IXa

a_H = 2.70 gauss (2H); H_1

a_H = 0.48 gauss (2H); H_V



Xa

a_H = 2.70 gauss (2H); H_1

a_H = 0.49 gauss (2H); H_A

Nenitzescu and his associates provided convincing chemical evidence that the four-carbon atom ring was *anti* to the dienophilic fragment.[6] The EPR spectra are consistent with only this structural assignment. Only two protons of the tricyclic fragment of semiquinone **Xa** are coupled, indicating the replacement of a pair of *anti* hydrogen atoms by the cyclobutane ring. Clearly, EPR spectroscopy may prove very valuable for the assignment of structure in compounds of this kind.[1]

The spectrum of **IXa** is modestly more complex than that of **Xa**. The introduction of the double bond yields an additional coupling as expected on the basis of an important interaction between the back lobe of the carbon-hydrogen bonding orbital of the *syn* proton and the *pi* bond. The assignments are based on this viewpoint.

The spectrum of **VIIIa** reveals an even greater delocalization of the spin density. Three groups of eleven, well resolved lines are observed in this instance. The spacing and intensity pattern (1:4:6:6:9:12:9:6:6:4:1) are compatible with a large hyperfine interaction of two equivalent protons (a_H = 0.44 gauss) and a smaller hyperfine interaction with four other protons (a_H = 0.14 gauss). The larger coupling constant is similar to the coupling constant of the vinyl protons in **Ia**, **VIa** and **IXa** and may be assigned with some confidence. The smaller coupling constant is similar to the coupling of the *syn* protons in **VIa** and **IXa**. Accordingly, one pair of the four equivalent couplings may be assigned to the *syn* protons of **VIIIa**. The second pair with the small coupling constant are presumably the vinyl protons (H_{V_2}). Thus, the results for the semiquinones examined in this study suggest that spin density may be propagated through one *pi* bond to the rear lobe of the *syn* protons or to another *pi* bond.

The delocalization mechanism and other examples of long range coupling are under study.

Acknowledgement.--Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

1. G. A. Russell and K. Y. Chang, J. Am. Chem. Soc., 87, 4381, 4383 (1965).
2. D. Kosman and L. M. Stock, ibid., 88, 843 (1966).
3. S. F. Nelsen and B. M. Trost, Tetrahedron Letters, 5737 (1966).
4. The investigation of several group labeled derivatives of Ia revealed that the bridgehead protons were not coupled.[3] The bridgehead protons in the bicyclo[2.2.2]octane derivatives discussed in this report are even closer to the nodal plane of the aromatic pi orbital and the coupling constants may be confidently assumed to be small.
5. The hydroquinones were prepared from the Diels-Alder adducts of benzoquinone with cyclohexadiene-1,3, [O. Diels and K. Alder, Ber., 62, 2337 (1929)], cyclooctatetraene, [W. Reppe, O. Schlichting, K. Klager, and T. Toepal, Ann., 560, 1 (1948)], and cyclooctatriene. The semiquinones were prepared by base-catalyzed air oxidation of the hydroquinones in acetonitrile solution. The spectra were recorded with Varian V4500 or E3 systems.
6. (a) M. Avram, G. M. Mateescu, and C. D. Nenitzescu, Ann., 636, 174 (1960).
   (b) M. Avram, E. Sliam, and C. D. Nenitzescu, ibid., 636, 184 (1960).