Photolysis of triphenyltin azide at −160° gave the corresponding nitrene which was observed by esr and may be a ground-state triplet with $D = 1.54$ and $E = <0.01$ cm^{-1}. This is the first direct physical evidence for the existence of a nitrene derived from a metal–azide type molecule. In contrast to the other pure azides studied, a strong $S = {}^1/_2$ resonance signal was also observed in the crystal. Repeated unsuccessful attempts were made to observe the triplet signal at −160° for the pure powdered triphenyltin azide and also for dilute solid solutions of the azide in several solvents.

The resonance signals for both *p*-fluorobenzenesulfonyl nitrene and triphenyltin nitrene bleached at about −35°.[10]

Photolysis of cyanuric triazide[11] at −160° yielded a ground-state triplet nitrene for which $D = 1.440$, $E = 0.005$ cm^{-1}. This nitrene displayed remarkable thermal stability. The resonance signal for the nitrene persisted with only slightly diminished intensity for *1 week at room temperature.*

Pure phenyl azide and methanesulfonyl azide were photolyzed in the glassy state at −160°. Strong nitrene resonance signals were observed which developed complicated sharp line structure upon increasing temperature; however, the integrated intensities remained nearly constant up to about −35°. In this temperature range rapid bleaching occurred for both these nitrenes. The measured D values (phenyl nitrene, $D = 0.999$, $E = 0$ cm^{-1}, and methanesulfonyl nitrene, $D = 1.569$, $E = 0$ cm^{-1}) were in substantial agreement with previously reported values.[4] Related bleaching experiments were performed on dilute randomly oriented glassy solutions of the azides.[4] We found that the bleaching temperatures for such solutions were invariably in the range of −120°. The relatively high bleaching temperatures for nitrenes in single crystals probably result from the fact that the nitrene is locked in a highly oriented environment in the crystalline lattice.

Comparison of variations in line width with increasing temperature is also instructive. The esr lines in the *p*-fluorobenzenesulfonyl nitrene and triphenyltin nitrene spectra were approximately 5 gauss wide (peak to peak derivative) at −160°. The triplet lines in the cyanuric nitrene spectra were only 1 gauss wide for a comparable crystal orientation. Thermal line broadening made esr measurements difficult above −100° for the hydrogen-containing single crystals and glasses, but the cyanuric nitrene esr lines were only 2 gauss wide at room temperature. This remarkable difference in both line width and thermal line width variation can be best ascribed to dipolar line-broadening effects of hydrogen. The dramatic line broadening above −100° in the hydrogen-containing materials is probably a preliminary to a nitrene–hydrogen abstraction reaction. The line broadening may result from motional effects due to hydrogen or may reflect some real conformational changes occurring in the materials.

The zero-field splitting parameter D is proportional to the magnitude of dipolar spin interaction between the two spin-unpaired electrons from the nitrogen atom of the nitrene.[12] In the case of phenyl nitrene one electron may occupy a π-molecular orbital involving the aromatic π-system; the other electron is localized in an orthogonal p-orbital on nitrogen. π delocalization reduces the spin density on nitrogen, and a decrease in the D value results.

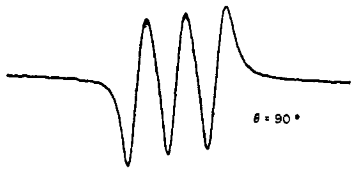

Figure 1. Derivative of the absorption (dX^{11}/dH) for *p*-fluorobenzenesulfonyl nitrene. The center of the three lines is at 8089 gauss for a microwave frequency of 9213 kMc/sec for the stated angle.

For the highly delocalized dinitrene derived from 1,4-diazidobenzene, a D value of 0.0675 cm^{-1} has been obtained. The D value for cyanuric nitrene, 1.440 cm^{-1}, is not particularly small. Delocalization of the π electrons on nitrogen between adjacent nitrene nitrogens is not possible due to their *meta* relationship.[13] The possibility of decomposition into simpler nitrenes such as cyanonitrene which might possess a large D value cannot be excluded.[14]

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[10] In order to eliminate errors introduced by spin lattice broadening all esr measurements on the thermally bleached samples were made after recooling the sample to −160°.

[11] G. J. King, F. F. Carlson, and B. S. Miller, *Bull. Am. Phys. Soc.*, **10**, 373 (1965).

[12] J. Higuchi, *J. Chem. Phys.*, **39**, 1847 (1963).

[13] A calculation is in progress to determine the extent of π delocalization in the cyanuric nitrene. The bond alternation for the ring is 1.31 and 1.38 A.

[14] We wish to thank a referee for calling our attention to this possibility.

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Electron Paramagnetic Resonance Spectra. III. Coupling Constants for Protons in Bicyclic Derivatives of Semiquinones[1]

Sir:

We have examined the epr spectra[2,3] of some unsaturated bicyclic semiquinone derivatives. Russell and Chang recently observed long-range stereoselective couplings for the saturated protons of bicyclic semidiones and pointed out that the vinyl protons of the semidione prepared from 3-ketobicyclo[3.2.1]octene-6 were coupled.[4] In this communication we report other long-range couplings to the protons bonded to unsaturated carbon atoms in bicyclic radicals.

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[1] Supported in part by the Petroleum Research Fund of the American Chemical Society (2325A4) and in part by the National Science Foundation (G25190).

[2] M. C. R. Symons, *Advan. Phys. Org. Chem.*, **1**, 183 (1963).

[3] A. Carrington, *Quart. Rev.* (London), **17**, 67 (1963).

[4] G. A. Russell and K. Y. Chang, *J. Am. Chem. Soc.*, **87**, 4381 (1965); G. A. Russell, K. Y. Chang, and C. W. Jefford, *ibid.*, 4383 (1965). We have also detected long-range couplings in the semiquinones of 3′,6′-dihydroxybenzobicyclo[2.2.1]heptene-2 and 3′,6′-dihydroxybenzobicyclo[2.2.2]octene-2. Our results are similar to the observations of Russell and Chang and will be discussed in a forthcoming publication.

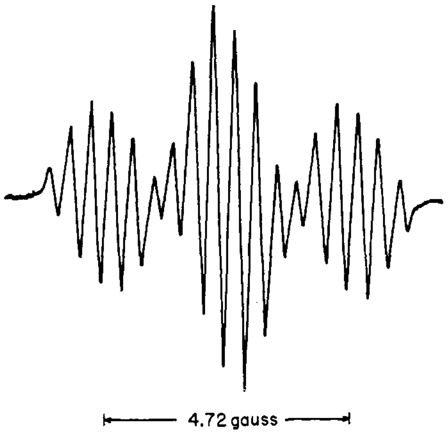
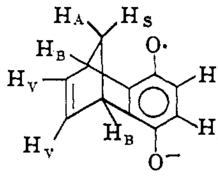


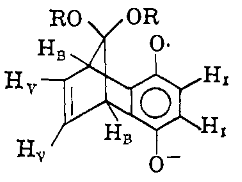
Figure 1. The epr spectrum of Ia in acetonitrile at ambient temperature.

The epr spectrum of the semiquinone (Ia)[5] prepared from 3′,6′-dihydroxybenzobicyclo[2.2.1]heptadiene-2,5 (I) reveals important spin density at the protons of the bicyclic fragment of the molecule.[6] The complexity of the spectrum of Ia, shown in Figure 1, prompted the preparation of group-labeled semiquinones IIa–IVa for a secure assignment of the coupling constants. The large coupling constant (about 2 gauss) for two protons in each radical is assigned to the aryl protons ($H_{\rm I}$) on the basis of the many results for other semiquinones. The spectrum of IIa wherein the *syn* and *anti* hydrogen atoms[7] of Ia are replaced by ethoxy substituents is much less complex. Radical anion IIa exhibits a triple resonance ($a_{\rm H} = 0.52$ gauss, intensity 1:2:1). The spectrum of IIa indicates selective coupling of either the bridgehead protons ($H_{\rm B}$) or the vinyl protons ($H_{\rm V}$). The spectrum of semiquinone IIIa with one vinyl proton is much simpler with coupling to only one proton of the bicyclic portion of the radical. Semiquinone IVa with one bridgehead proton and two vinyl protons has an epr spectrum indicative of coupling to two nonequivalent protons. These observations reveal that the vinyl protons (rather than the bridgehead protons) in IIa–IVa are coupled.[8]



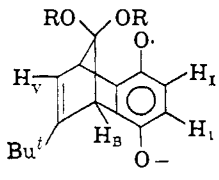
Ia

$a_{\rm H} = 2.36$ gauss (2 H); $H_{\rm I}$
$a_{\rm H} = 0.80$ gauss (1 H); $H_{\rm A}$
$a_{\rm H} = 0.40$ gauss (3 H); $H_{\rm S}$,$H_{\rm V}$



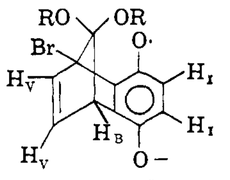
IIa ($R = C_2H_5$)

$a_{\rm H} = 2.38$ gauss (2 H); $H_{\rm I}$
$a_{\rm H} = 0.52$ gauss (2 H); $H_{\rm V}$



IIIa ($R = -CH_2CH_2-$)

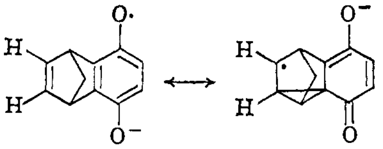
$a_{\rm H} = 2.34$ gauss (2 H); $H_{\rm I}$
$a_{\rm H} = 0.52$ gauss (1 H); $H_{\rm V}$



IVa ($R = CH_3$)

$a_{\rm H} = 2.05$ gauss (2 H); $H_{\rm I}$
$a_{\rm H} = 0.86$ gauss (1 H); $H_{\rm V}$
$a_{\rm H} = 0.46$ gauss (1 H); $H_{\rm V}$

The three-bond coupling constant of the vinyl protons of the bicyclic radical anions is remarkably large when contrasted with other spectroscopic results. For example, $a_{\rm H}$ for the protons of the *t*-butyl group of 2,5,-di-*t*-butylsemiquinone is about 0.06 gauss.[9] The transfer of spin density to the vinyl protons either by the overlap of the aryl molecular orbital and the carbon–hydrogen bond orbital or by rapid electron transfer cannot be excluded at present. However, it seems more likely that the spin density is transferred *via* the overlap of the aryl molecular orbital with the π-bond orbital, as illustrated in the valence bond structures. Work is in progress to determine the sign of the coupling constant to verify this interpretation.



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[5] The semiquinones were prepared from the corresponding hydroquinones by air oxidation in the presence of base in acetonitrile or dimethyl sulfoxide. A Varian V4500 instrument was used to record the spectra. The synthetic methods and pertinent physical and spectroscopic properties of the hydroquinones confirming the structures will be reported later. However, we wish to acknowledge the sample of the Diels–Alder adduct of benzoquinone and cyclopentadienone diethyl ketal from Eaton and Hudson and the sample of 3-*t*-butylcyclopentadienone dimethylene ketal from Garbish used as starting materials.

[6] The spectroscopic results are summarized under each structure as $a_{\rm H}$, the coupling constant, and the number of protons that exhibit the coupling constant. The assignment that follows the experimental observations is based on the differences in the spectra of Ia–IVa.

[7] The assignment of $a_{\rm H_A} = 0.80$ gauss and $a_{\rm H_S} = 0.40$ gauss in Ia is based on the observations of Russell and Chang (ref 4). We are now examining the spectrum of hydrocarbon anion radicals, *i.e.*, derivatives of benzonorbornadiene, to confirm these assignments.

[8] Russell and Chang[4] find that the coupling constants for the bridgehead protons in the bicyclo[2.2.1]heptane semidiones are observable and not always small compared to the couplings of the other protons.

[9] G. K. Fraenkel, *Ann. N. Y. Acad. Sci.*, 67, 546 (1957).

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Sulfur Dioxide Insertion. II. S-Sulfinatopentacarbonylmanganese(I) Complexes[1]

Sir:

It was recently demonstrated in these laboratories that cyclopentadienylalkyl- and -aryliron dicarbonyls react readily with liquid sulfur dioxide to give cyclopentadienyliron dicarbonyl S-sulfinato[2] complexes, $C_5H_5Fe(CO)_2(SO_2R)$.[1] Subsequently, the SO_2 insertion was extended to dialkyl- and -arylmercury compounds and to cyclopentadienyl(methyl)molybdenum tricarbonyl.[3] It therefore became of considerable interest to evaluate the scope of this reaction and to show (1) whether the product is invariably a sulfinato-

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[1] For part I of this series, see J. P. Bibler and A. Wojcicki, *J. Am. Chem. Soc.*, 86, 5051 (1964).

[2] To systematize the nomenclature these complexes will be referred to henceforth as sulfinates (S-sulfinates if M–S bonding is present) rather than sulfonyls.

[3] A. Wojcicki and J. P. Bibler, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 36M.