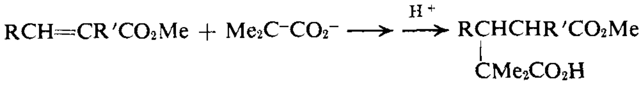
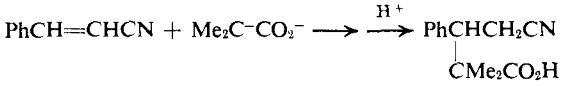


$$RCH{=}CR'CO_2Me + Me_2C^{-}CO_2^{-} \longrightarrow \xrightarrow{H^+} \underset{\displaystyle CMe_2CO_2H}{RCHCHR'CO_2Me}$$

III

The dianion of isobutyric acid caused the polymerization of acrylonitrile and crotononitrile even at −78°. However, cinnamonitrile formed the Michael adduct at



$$PhCH{=}CHCN + Me_2C^{-}CO_2^{-} \longrightarrow \xrightarrow{H^+} \underset{\displaystyle CMe_2CO_2H}{PhCHCH_2CN}$$

room temperature. The dianion of isobutyric acid and crotonaldehyde or cinnamaldehyde underwent 1,2 addition.[9,10]

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health (Grant No. GM 16594). Dean P. Stull checked several of the dianion reactions.

[9] G. M. Moersch and A. R. Burkett, *J. Org. Chem.*, **36**, 1149 (1971).

[10] Satisfactory microanalytical data and/or nmr and mass spectral data were obtained for all new compounds.

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Received August 30, 1971

Long-Range Interactions in 6-Nitro- and 6,7-Dinitrobenzonorbornene Anion Radical and Related Radicals

Sir:

Many esr studies of the norbornene system having spin-labeled groups, such as semidiones,[1] semiquinones,[2] and semifuraquinones,[3] have been reported hitherto and the long-range hyperfine splittings of these compounds discussed in relation to their stereochemistry.[4] All of these anion radicals have structures in which the spin-labeled groups are bounded by two equivalent carbon atoms of the bridged bicyclene.

One of the most interesting current problems in bridged bicyclic systems is that of long-range coupling to the anti and exo hydrogens, and it is toward an understanding of this that we have investigated the esr of unsymmetrical nitrobenzonorbornene and symmetrical dinitrobenzonorbornene. Mono- and dinitrobenzonorbornene anion radicals and related radicals were prepared *in situ* from the parent compounds by reduction with propiophenone in DMSO containing potassium *tert*-butoxide.[5]

The esr spectrum of 6-nitrobenzonorbornene anion radical (**1**) is shown in Figure 1. The assignment of the hyperfine splitting constants (hfsc's) of the hydrogen atoms in **1** was established by the experimental data[6] for 6-nitrobenzonorbornen-2-one (**2**) and -9-one (**3**) anion radicals, and is based on the results of Russell,[1] Stock,[2] Nelsen,[3] Geske,[7] and Tori,[8] and coworkers.

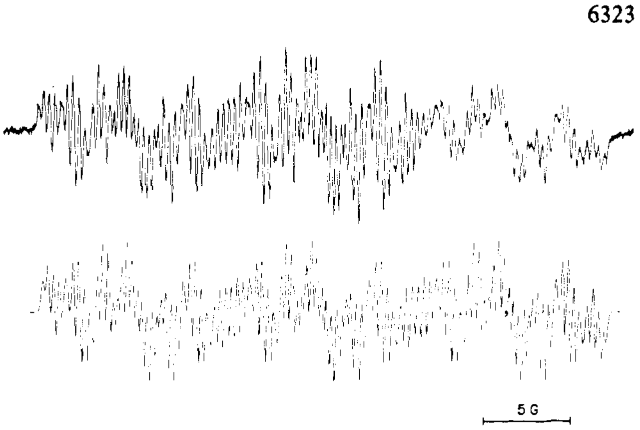
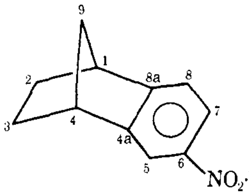


Figure 1. Top: first-derivative esr spectrum observed in the reduction of 6-nitrobenzonorbornene with propiophenone in the presence of potassium *tert*-butoxide in DMSO solution at 25° by a Varian V4502-15 spectrometer. Bottom: calculated spectrum with Gaussian line width of 0.23 G and hfsc's given in the text.



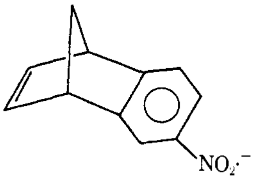
1

$a^N = 10.63$ (1 N) $a^{H_8} = 1.09$ (1 H)
$a^{H_o} = 3.66$ (1 H) $a^{H_1} = 0.63$ (1 H)
$a^{H_o} = 3.14$ (1 H) $a^H = 0.37$ (1 H)
$a^{H_{exo\text{-}2}} = 1.46$ (1 H) $a^H = 0.24$ (2 H)

The interesting point is that the hfsc of the exo-C-2 (homo–para–exo) hydrogen is very large, but that of the exo-C-3 (homo–meta–exo) hydrogen atom is rather small. This result gives evidence that the hfsc's of hydrogens in this system are mainly affected by the spin density at the para and meta positions of the nitrobenzene anion radical. The magnitudes of these long-range interactions are not, however, exactly proportional to the spin density of the benzene ring. This may be the result of an additional interaction mechanism being involved.

The magnitude of the splitting of anti-C-9 hydrogen will be either 0.37 or 0.24 G,[9] and although we could not determine which is the correct value, it is in either case small. We believe that the long-range interaction at this position is attributed to a W-plan arrangement from the p_z orbitals of both the 4a and 8a carbon atoms, but that cancelation by the opposite signs of the spin density at these positions results in this value becoming small.

The spectrum of 6-nitrobenzonornbornadiene anion radical (**5**) was analyzed as follows.



5

$a^N = 10.35$ (1 N) $a^H = 0.44$ (2 H)
$a^{H_o} = 4.08$ (1 H) $a^H = 0.26$ (1 H)
$a^{H_o} = 2.83$ (1 H) $a^H = 0.19$ (2 H)
$a^{H_8} = 1.15$ (1 H)

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[1] (a) G. A. Russell and K.-Y. Chang, *J. Amer. Chem. Soc.*, **87**, 4381 (1965); (b) G. A. Russell, G. W. Holland, K.-Y. Chang, and L. H. Zolkow, *Tetrahedron Lett.*, 1955 (1967); (c) G. A. Russell and P. R. Whittle, *J. Amer. Chem. Soc.*, **89**, 6781 (1967).

[2] (a) D. Kosman and L. M. Stock, *ibid.*, **88**, 843 (1966); (b) *Chem. Commun.*, 551 (1968); (c) *J. Amer. Chem. Soc.*, **91**, 2011 (1969).

[3] S. F. Nelsen and E. D. Seppanen, *ibid.*, **89**, 5740 (1967).

[4] G. R. Underwood and V. L. Vogel, *ibid.*, **93**, 1058 (1971).

[5] G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964).

[6] $a^H = 1.46$ G disappeared in **2**, while $a^H = 0.63$ G was observed in **3**. The assignment of the hfsc's of the ortho hydrogens using 7-deuterio-6-nitrobenzonorbornene is in progress. The coupling of homo–para–exo hydrogens of 6-nitrobenzobicyclo[2.2.2]octene anion radical was determined to be the same as that of the meta hydrogen: R. Konaka and S. Terabe, unpublished results.

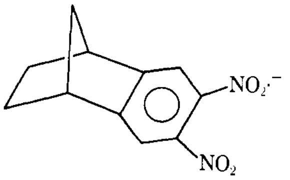
[7] D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 125 (1967).

[8] For the observation of the contact shift of the 6-aminobenzonorbornene complex with bis(acetylacetonato)nickel(II), see K. Tori, Y. Yoshimura, and R. Muneyuki, *J. Amer. Chem. Soc.*, **93**, 6324 (1971).

[9] These couplings are not those of the endo-C-2 or endo-C-3 hydrogens, since the spectrum of *endo,endo*-2,3-dideuterio-6-nitrobenzonorbornene anion radical (**4**) was the same as that of **1**.

Of interest is the finding that the difference between the hydrogen couplings of the ortho positions in **5** is larger than it is in **1**, presumably owing to the difference in the strain of the bridged bicyclic skelton.

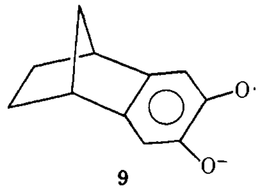
The spectrum of 6,7-dinitrobenzonorbornene anion radical (**6**) was obtained, and its assignment is based on the observation[10] of the spectra of 5,8-dideuterio-(**7**) and *exo,exo*-2,3-dideuterio-6,7-dinitrobenzonorbornene anion radicals (**8**). The coupling of the anti-C-9 hydrogen was determined to be less than 0.4 G from the line width of **6**. In the symmetrical norbornene anion radical system, the anti hydrogen atom lies on the symmetrical plane which bisects the spin-labeled component, so the magnitude of the anti-C-9 hydrogen coupling can be elucidated by the orbital symmetry theory.[1c,11] The opposite signs of the highest occupied molecular orbital coefficients for C-4a and C-8a in systems such as the *p*-semiquinone[2] prevent the delocalization of the unpaired spin into the C-9 methylene position, since the form $a^H = Q(c_{4a} + c_{8a})^2$ is taken.[12] In contrast, the semidione system having the same sign shows a large coupling at the anti hydrogen.[1] In a similar manner, we conclude that because of the anti symmetry of **6**, the anti-C-9 hydrogen coupling is considerably small.



6

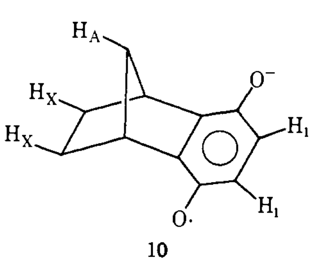
$a^N = 2.91$ (2 N)
$a^{H_{exo\text{-}2,3}} = 0.64$ (2 H)
$a^{H_{anti\text{-}9}} < 0.4$

In order to make additional confirmation of the orbital symmetry theory in a symmetry system other than the semidione system, we prepared norbornyl *o*-semiquinone (**9**). As **9** has the same sign at C-4a and C-8a, it is predicted that the value of anti-C-9 hydrogen coupling in **9** will be greater than it is in **6** or in norbornyl *p*-semiquinone (**10**).[2c] From the spectrum of **9**, the anti-C-9 hydrogen coupling was determined to be 3.10 G. The validity of the symmetry theory was established by the fact that the ratio of the anti-C-9 hydrogen hfsc of **9** to that of **10** is much larger than the ratio of the C-4 hydrogen hfsc of *o*-semiquinone itself[13] to the hydrogen hfsc of *p*-semiquinone itself.[13]



9

$a^{H_{anti\text{-}9}} = 3.10$ (1 H)
$a^H = 1.09$ (2 H)
$a^H = 0.96$ (4 H)



10

$a^{H_1} = 2.50$ (2 H)
$a^{H_X} = 0.70$ (2 H)
$a^{H_A} = 0.70$ (1 H)

Acknowledgment. The authors are grateful to Drs. H. Tanida and R. Muneyuki of this laboratory for kindly donating the parent compounds **1**, **2**, **3**, **4**, and **6**, to Dr. K. Nishikida and Mr. S. Sakata for their assistance in obtaining the esr spectra, and to Dr. K. Tori for helpful discussion.

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(10) A coupling of 0.64 G was observed in **7** and not in **8**.

(11) G. A. Russell, T. Ku, and J. Lokensgard, *J. Amer. Chem. Soc.*, **92**, 3833 (1970). In this reference, the difference between a spin delocalization mechanism and a spin polarization mechanism is discussed with regard to the magnitude and stereoselectivity of long-range splittings.

(12) D. H. Whiffen, *Mol. Phys.*, **6**, 224 (1963).

(13) *o*-Semiquinone, $a^{H_{4,5}} = 3.65$ G (in ethanol); *p*-semiquinone, $a^{H_{2,3,5,6}} = 2.37$ G (in ethanol): G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 1333 (1961).

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Proton Contact-Shift Study of 6-Aminobenzonorbornene and 6-Aminobenzonorbornadiene[1]

Sir:

The mechanism of long-range hyperfine splittings (hfs) across σ bonds observed in the esr spectra of charged radicals of various types of rigid bicyclic and polycyclic compounds[2-6] has been a subject of controversy in recent years.[2-7] As an aid to understanding spin delocalization mechanisms, the esr technique is known to suffer from the disadvantage that only the magnitude and not the sign of hfsc's can be determined.[7b] A pmr technique[8] has been used to determine several signs of hfsc's in bicyclic nitroxide free radicals,[9] but there still remain difficulties in preparation of sufficiently stable and concentrated solutions of such free radicals.[9a]

Applications of the paramagnetic contact shift (cs)[8b,10] using bis(acetylacetonato)nickel(II), Ni(acac)$_2$,[11] have recently been highlighted in nmr spectroscopy for the investigation of electron spin distribution transmitted through σ orbitals.[12] We present here a proton

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(3) (a) D. Kosman and L. M. Stock, *ibid.*, **88**, 843 (1966); (b) *ibid.*, **91**, 2011 (1969), and references therein.

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(6) T. M. McKinney, *J. Amer. Chem. Soc.*, **90**, 3879 (1968).

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(8) (a) K. H. Hausser, H. Brunner, and J. C. Jochims, *Mol. Phys.*, **10**, 253 (1966); (b) E. de Boer and H. van Willigen, *Progr. NMR Spectrosc.*, **2**, 111 (1967).

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