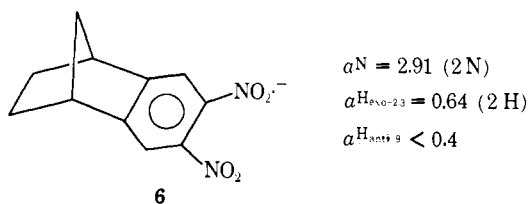


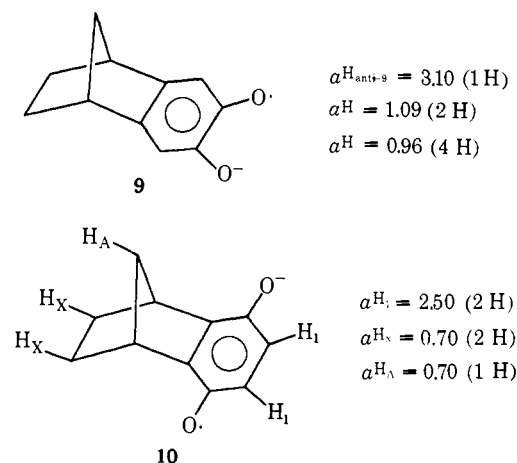
Of interest is the finding that the difference between the hydrogen couplings of the ortho positions in **5** is larger than it is in **1**, presumably owing to the difference in the strain of the bridged bicyclic skeleton.

The spectrum of 6,7-dinitrobenzonorbornene anion radical (**6**) was obtained, and its assignment is based on the observation¹⁰ 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.^{10,11} The opposite signs of the highest occupied molecular orbital coefficients for C-4a and C-8a in systems such as the *p*-semiquinone² 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.

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

(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.

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of **9** to that of **10** is much larger than the ratio of the C-4 hydrogen hfsc of *o*-semiquinone itself¹³ to the hydrogen hfsc of *p*-semiquinone itself.¹³

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(13) *o*-Semiquinone, $a^{H_{4,6}} = 3.65$ G (in ethanol); *p*-semiquinone, $a^{H_{2,4,6,8}} = 2.37$ 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-Aminobenzonorbornadiene¹

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 compounds²⁻⁶ 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 technique⁸ 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.

(4) (a) S. F. Nelsen and B. M. Trost, *Tetrahedron Lett.*, 5737 (1966); (b) S. F. Nelsen and E. D. Seppanen, *J. Amer. Chem. Soc.*, **89**, 5740 (1967); (c) *ibid.*, **92**, 6212 (1970); (d) S. F. Nelsen and P. J. Hintz, *ibid.*, **92**, 6215 (1970).

(5) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967).

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(7) (a) G. R. Underwood and R. S. Givens, *ibid.*, **90**, 3713 (1968); (b) G. R. Underwood and V. L. Vogel, *ibid.*, **93**, 1058 (1971), and references therein.

(8) (a) K. H. Hauser, 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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(12) (a) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, **92**, 1267 (1970); (b) I. Morishima, T. Yonezawa, and K. Goto, *ibid.*, **92**, 6651 (1970); (c) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *Chem. Commun.*, 1535 (1970); (d) I. Morishima, K. Okada,

cs study of 6-aminobenzonorbornene (**1**), its endo-2-, endo-3- and exo-2,exo-3-dideuterio derivatives (**2** and **3**, respectively), 6-aminobenzonorbornadiene (**4**), and 5-amino-*cis*-1,3-dimethylindane (**5**),¹³ complexed with Ni(acac)₂ at their nitrogen lone pairs in CDCl₃.

Figure 1 shows the proton cs data^{14,17} obtained in the usual manner.^{11,12,18} The relative cs values are in good agreement with those for hfsc's obtained by esr studies of anion radicals of the corresponding nitro derivatives done in this laboratory (see Figure 1).¹⁹ We have determined not only the sign, but also the assignments of hfsc's remaining undetermined. Moreover, the cs study disclosed relatively smaller values with unambiguous assignments. The downfield cs (positive sign) is due to positive spin density and the upfield cs (negative sign) may result from negative spin density.^{12,17}

The cs behaviors of the aromatic and the bridgehead protons of all the compounds examined were found to be similar to those obtained for toluidines.¹⁸ Therefore, the relatively lower negative and higher positive π spin densities are delocalized onto C-4a and C-8a (meta and para to the amino group), respectively,^{12b} by a π delocalization mechanism.^{10,18}

These spin densities on C-4a and C-8a in **2** are reflected in the small upfield and the large downfield cs values for H_{3x} and H_{2x}, respectively, both of which lie in the W-plan arrangement with the p π orbitals of C-4a and C-8a, respectively;²⁰ these facts imply that a mechanism of electron spin delocalization through σ orbitals is operative.¹² On the other hand, the cs values of H_{2n} and H_{3n} in **3**, both of which lie in the *folded* path, are nega-

M. Ohashi, and T. Yonezawa, *Chem. Commun.*, 33 (1971); (e) M. Ohashi, I. Morishima, K. Okada, T. Yonezawa, and T. Nishida, *ibid.*, 34 (1971).

(13) The compounds used in this study were synthesized from their corresponding nitro derivatives by reduction with Pd/C and showed satisfactory elemental analyses as *p*-nitrobenzamides. Protons H_{exo}, H_{endo}, H_{anti}, and H_{syn} are abbreviated as H_x, H_n, H_a, and H_s, respectively. The numbering for **5** used in this paper (see Figure 1) is convenient for the purpose of comparison.

(14) The pmr spectra were recorded on a Varian HA-100 spectrometer in the frequency-swept and TMS-locked mode, using about 0.8 M solutions of the compounds.

Signals in the initial spectra of uncomplexed **1-4** were assigned similarly to those of benzonorbornene, benzonorbornadiene,¹⁵ and their 6-methoxy derivatives.¹⁸ The H_{9a} and H_{9s} signals (doublets of triplets at δ 2.40 and 1.07 ppm, respectively) in the spectrum of uncomplexed **5** were readily assigned from $J_{9a-1(4)}$ and $J_{9s-1(4)}$ values (6.8 and 10.0 Hz, respectively).

In the spectra of **1-4** complexed with Ni(acac)₂, the H₁ and H₄ signals, which initially coincided and then were separated by the paramagnetic shifts due to Ni(acac)₂, were assigned on the basis of their signal broadening caused by paramagnetism;¹⁰ the signals due to H₄, which must be closer to the paramagnetic center than H₁ is, become broader than those due to H₁ as the Ni(acac)₂ concentration is increased. The assignments of the H₂ and H₃ signals were confirmed by spin-decoupling experiments, in which the H₁ and H₄ signals which were sufficiently separated by the paramagnetic shifts were successively irradiated.

The assignments of the H₁ and H₄ signals in the spectra of complexed **5** were made by removing the benzylic spin couplings on double irradiation of the aromatic H₈ and H₅ signals, respectively.

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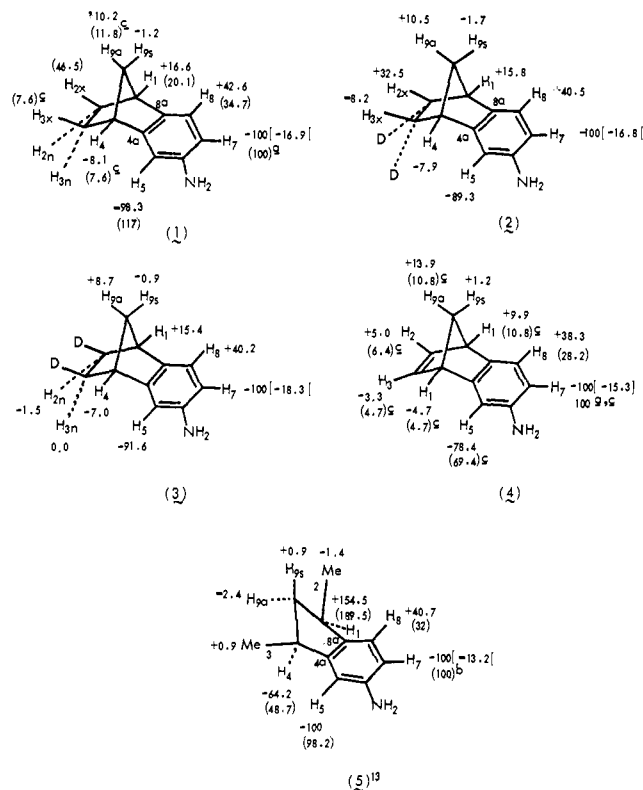


Figure 1. Relative values for proton contact shifts due to Ni(acac)₂ (values in square brackets are absolute shift values in parts per million at a 0.5 molar ratio of Ni/ligand)^{14,17} and relative values of hfsc's obtained with anion radicals of the corresponding nitro derivatives (in parentheses).¹⁹ ^a Taken from ref 19c. ^b Taken from ref 19a. ^c Tentatively assigned by the present authors.

tive and very small due to a σ spin polarization mechanism.^{12c,d} Similarly, H_{9a} in the W-plan arrangement with the benzene π system in **1-3** evidently shows a downfield cs resulting from the σ spin delocalization, whereas the cs value for H_{9s} implies a spin polarization mechanism; the relatively smaller cs values are attributable to the opposite signs of spin densities induced on C-4a and C-8a, although the higher positive density on the latter evidently has an effect. These results are considered to offer experimental support for the theoretical study of anion radicals of bicyclic semidiones.^{7b}

In compound **4**, the cs values for the vinyl H₂ (downfield) and H₃ (upfield) indicate that the negative and positive π spin densities are transmitted onto C-2 and C-3 from C-8a and C-4a, respectively, by a π delocalization mechanism through direct homoconjugation.^{2b,3a,4a} Thus, the downfield cs of H_{9s}, which lies in the W-plan arrangement with the p π orbitals of the olefinic carbons, can be interpreted as due mainly to the σ spin delocalization from C-2, as was previously suggested.^{4a} However, the fact that both cs values for H_{9a} and H_{9s} are more positive in **4** than in **1-3** might not entirely exclude an alternative explanation that the strain from the double bond is responsible for the effects, as was previously suggested from esr studies on bicyclic semidiones.^{2b}

That the cs values for H₁ and H₄ are smaller in **4** than in **1-3** may be due to the change in molecular geometry by the introduction of the double bond. The very large cs values for H₁ and H₄ in **5** in comparison with those in **1-4** can readily be understood by the stronger hyperconjugation between the C-H bonds and the benzene

π system due to their *axial* nature, which is apparent from the $J_{9a,1(4)}$ and $J_{9s,1(4)}$ values.¹⁴ As can be expected from the molecular conformation of **5**, the ρ_s values for the methyl protons, H_{9a} , and H_{9s} were very small.

In conclusion, it is suggested that the sign of the hfsc of a proton with a $p\pi$ orbital across the W-plan arrangement is the same as the sign of the π spin density.

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Organometallic Chalcogen Complexes. XXIII. Preparation and Structural Characterization of a Mixed Transition Metal Cluster Complex, $[\text{Re}_2\text{Mo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3](\text{S})[\text{SMo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3]$, Containing Triply and Quadruply Bridging Sulfur Atoms. A New Synthetic Route to Highly Clustered Metal-Sulfur Systems¹

Sir:

The extreme versatility of sulfur in atomic form in its various modes of coordination in organometallic cluster systems has been established directly from crystallographic studies which have shown a "bare" sulfur atom linked to transition metals as (1) a doubly bridging, two-electron σ -donating ligand;² (2) a triply bridging, four-electron σ -donating ligand;³ (3) a quadruply bridging, four-electron σ -donating ligand;⁴ and (4) a quadruply bridging six-electron σ -donating ligand.⁵ Similar metal linkages have also been found for atomic selenium and tellurium. Although a variety of reactions have been used to prepare such organometallic chalcogen complexes, in many cases they are obtained mostly in low yields from rather unusual and sometimes unpredicted reactions. In an effort to acquire them in a more designed fashion, we are carrying out reactions by which reactive organometallic chalcogen intermediates can be isolated and then brought by further reaction to produce desired metal cluster chalcogen species.

Abel and coworkers⁶ first studied the reactions of organotin-mercaptop complexes of the types $\text{R}_3\text{SnSR}'$ and $\text{R}_2\text{Sn}(\text{SR}')_2$ with organometallic halides to produce compounds containing the mercaptan as a ligand, the driving force being the formation of a metal-sulfur bond and an organotin halide. It was subsequently shown by Schumann and coworkers⁷ that the chalcogen atom in $(\text{Me}_3\text{Sn})_2\text{X}$ (where X = S, Se, Te) is sufficiently basic to displace a carbonyl ligand from $\text{M}(\text{CO})_6$

(where M = Cr, Mo, W) to form $\text{M}(\text{CO})_5(\text{X}(\text{SnMe}_3)_2)$ (where X = S, Se, Te). We have undertaken a systematic study of the reactions of $(\text{Me}_3\text{Sn})_2\text{S}$, both in the free state and bound to a metal as a Lewis base adduct, with a variety of organometallic halides. In order to illustrate the diversity and scope of this method, including the means of preparing mixed metal-sulfur clusters, we report here the synthesis and structural analysis of one of the first mixed metal-sulfur complexes, $[\text{Re}_2\text{Mo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3](\text{S})[\text{SMo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ (**1**), which is of special interest in its hitherto unknown feature of possessing both triply bridging, four-electron σ -donating and quadruply bridging, six-electron σ -donating sulfur atoms.

The reaction of $(\text{Me}_3\text{Sn})_2\text{S}$ with $\text{Re}(\text{CO})_5\text{Cl}$ was previously reported by one of us to go smoothly to a bridged dimeric species, $[\text{Re}(\text{CO})_4(\text{SSnMe}_3)]_2$.⁸ This Me_3SnS -bridged dimer reacts with $\text{Mo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cl}$ in either 1,2-dimethoxyethane or benzene at 75° with loss of carbonyl to form **1**. This air-stable compound, which is only slightly soluble in polar solvents, was shown from a magnetic susceptibility measurement⁹ to be diamagnetic. Its stoichiometry¹⁰ as well as atomic arrangement were ascertained from a crystallographic investigation.

Crystals of **1** suitable for X-ray diffraction were taken from the reaction product and were found from photographic data to belong to the monoclinic system. The unit cell of centrosymmetric symmetry $P2_1/c$ contains four molecules. The lattice parameters obtained from application of a diffractometric method¹¹ are $a = 9.364$ (1), $b = 30.256$ (3), $c = 11.015$ (1) Å, $\beta = 122.52$ (1)°. The structure was determined by conventional Patterson and Fourier techniques from intensity data collected with Mo $K\alpha$ radiation by the θ - 2θ scan technique on a General Electric full-circle, Datex-controlled diffractometer. A mixed anisotropic-isotropic, full-matrix, least-squares refinement based on 2224 absorption-corrected data with $|F| > 4\sigma(F)$ yielded an unweighted R_1 value of 4.3%. In this refinement, each of the two cyclopentadienyl rings was constrained as a rigid regular D_{5h} pentagon with C-C and C-H bond lengths of 1.405 and 1.09 Å, respectively. Anisotropic thermal parameters were utilized for the metal and sulfur atoms and isotropic ones for all other atoms, with those of the hydrogen atoms not varied throughout the refinement.¹²

The molecular geometry (Figure 1) of **1** consists of a nonlinear trinuclear metal framework with $\text{Re}(\text{I})$ of the central $\text{Re}(\text{CO})_3$ fragment forming electron-pair metal-metal bonds with a $\text{Re}(\text{CO})_3$ group and a $\text{Mo}(h^5\text{-C}_5\text{H}_5)(\text{CO})_2$ group. The three metal atoms of this open triangular system are all bridged on one side of their plane by a "bare" sulfur atom, S(1), and on the

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(10) Yield >60% based on S. *Anal.* Calcd for $\text{Re}_2\text{Mo}_2\text{O}_2\text{S}_2\text{C}_{21}\text{H}_{10}$: Mo, 17.99; S, 6.02; C, 23.65; H, 0.94. Found: Mo, 17.30; S, 5.98; C, 24.23; H, 1.00; mp, 290° dec.

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