Table IX. Average Net Atomic Charges from Extended L-Shell Refinement

Water Molecule (HF Basis Set)

	Oxalic acid	Nickel complex			Av
O	−0.25	−0.22	−0.26	−0.19	−0.22
H	+0.20	+0.20	+0.20	+0.24	+0.20
H	+0.25	+0.14	+0.18	+0.20	

Carbonyl Oxygen Atom

Cyanuric acid		Oxalic acid	Nickel complex	
HF	STO			
−0.12	−0.07	−0.25	−0.31	−0.43
−0.24	−0.22	−0.30		

ethyl)malondiamidato]nickel(II) and oxalic acid crystals show very similar atomic charges (Table IX). A similar comparison can be made between carbonyl oxygens in oxalic acid, the nickel complex, and cyanuric acid (Table IX). Since the carbonyl groups are attached to different molecules, less close agreement is expected.

It is clear that a large amount of chemical information can be obtained from experimental atomic charges. Perhaps the most challenging results are the small positive charge on the nickel atom and the asymmetric charge distribution in the perylene moiety of the perylene–TCNE complex.

The deformation parameters from the one-center model provide a less obvious picture and it is quite likely that different results will be obtained when the two-center overlap terms are included in both the theoretical and experimental treatments.

The correlations between parameters observed in the extended L-shell refinement when the scale factor is included as a parameter indicate the desirability of a sufficiently accurate experimental determination of the scale factor.

We conclude that with further improvements in experimental and computational techniques (such as collection of accurate data at liquid helium temperatures and the inclusion of two-center terms in the model), a whole new area is becoming accessible to X-ray crystallographic methods.

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Application of Simple Theoretical Methods to the Solution of Chemical Problems. IV.[1] Hydrogen, Carbon-13, and Oxygen-17 Hyperfine Splitting Constants in Rigid Bicyclic Semidiones

Graham R. Underwood* and Veronica L. Vogel

Contribution from the Department of Chemistry,
New York University, University Heights, Bronx, New York 10453.
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Abstract: An examination is made of the usefulness of the INDO-SCF molecular orbital method as a means of calculating long-range epr coupling constants and factoring them into the components due to various spin delocalization mechanisms. The rigid bicyclic semidione radical anions are employed as models. Satisfactory agreement is obtained between the experimental and calculated hfsc's for hydrogen and carbon atoms, although no attempts were made to optimize the geometry of the radicals. Several possible spin delocalization mechanisms are discussed and it is concluded that opposing mechanisms are operative, particularly for the γ protons, and that further application of this approximate theory should be of value.

The fine details of electron spin interactions in paramagnetic molecules or radicals and diradicals are of considerable interest in many aspects of radical reactions and reactivity, photochemistry, nmr and esr, etc. The nature of these interactions can be deduced to a certain extent from the dependence of the magnitude of the epr hyperfine splitting constant (hfsc) on the geometry of the radical or radical ion under investigation.[1,2] Experimentally, changes in geometry can be effected by substitution or, more satisfactorily, by forcing the radical to assume a rigid structure as a result of bridging within the molecule, the latter having recently been achieved for bicyclic and polycyclic radicals.[3-6] There are, however, some limitations inherent in trying to use these methods to predetermine the geometry of a radical. Upon substitution in flexible radicals, the exact conformer population is not known, possibly resulting in ambiguous or misleading interpretations.[7] Also, the substitution of a hydrogen by an alkyl group may have consequences

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other than just simply changing the geometry or conformational population.[8] When a molecule is forced to assume a rigid structure, ring strain and substitution may likewise introduce perturbations of an unknown magnitude. In addition, the esr technique suffers from the disadvantage that only the magnitude and not the sign of the hfsc can be determined. Several techniques have been used to determine the sign of the hfsc but in spite of significant advances in this field,[9–13] several deficiencies still exist.

Owing to these experimental problems we have elected to use theoretical methods to examine the relative importance of the various possible mechanisms of spin delocalization to distant hydrogens. Although this approach eliminates most of the experimental difficulties, doubts must be raised as to the validity of the calculations and, therefore, it is first necessary to test adequately the ability of the theoretical method to reproduce reliable experimental data. A large number of long-range hfsc's have been observed in the semidiones and, as the identity of this class of radicals is well established,[14] they appear to constitute a suitable series for this purpose.[15]

We have previously used the extended-Hückel method[16] in an attempt to calculate long-range hfsc's in the semidiones[8] and, while reasonable agreement between experimental and calculated hfsc's was obtained, serious objections could be raised against using such calculations as a basis for an evaluation of spin delocalization mechanisms. Primarily the extended-Hückel method is incapable of predicting spin densities resulting from spin polarization. This is a particularly serious defect in this context, for it is known that spin polarization is the predominant mechanism giving rise to electron spin at the atomic nuclei in planar aromatic molecules.[17] Further, the limited experimental evidence indicates that many long-range hfsc's result primarily from the effects of spin polarization.[18] It is therefore a dichotomy that the extended-Hückel method was able to reproduce the magnitude of most of the large long-range hfsc's in the semidiones without taking spin polarization into account.

We have chosen to use the INDO–SCF approximation[19] to examine the spin delocalization mechanisms in these radicals, since this method explicitly includes one-center exchange integrals and thus quantitatively introduces the effect of Hund's rule on a molecular scale. In examining this method, Pople and coworkers have obtained excellent agreement between experimental and calculated α-proton hfsc's for a large number of planar radicals where spin polarization is important.[19] These workers, however, did not extend their calculations to the more interesting question of long-range hfsc's.[20]

The INDO Method

The details of the INDO method have been discussed previously[19] and here we summarize only the pertinent details. The unrestricted wave function for a radical with a electrons of α spin and b electrons of β spin ($a > b$) is of the form

$$\Psi = |\psi_1^{\alpha}(1)\alpha(1)\psi_2^{\alpha}(2)\alpha(2)\ldots \psi_a^{\alpha}(a)\alpha(a)\psi_1^{\beta}(a+1)\beta(a+1)\ldots \psi_b^{\beta}(a+b)\beta(a+b)|$$

where ψ_i^{α} and ψ_i^{β} are assumed to be linear combinations of valence-shell atomic orbitals

$$\psi_i^{\alpha} = \sum_{\mu} c_{\mu i}^{\alpha}\phi_{\mu}$$

$$\psi_i^{\beta} = \sum_{\mu} c_{\mu i}^{\beta}\phi_{\mu}$$

In solving this set of equations for $c_{\mu i}^{\alpha}$ and $c_{\mu i}^{\beta}$ by the standard self-consistent-field method, certain approximations of atomic and molecular integrals must be made. In the INDO approximation, differential overlap is neglected for all polycenter interelectron repulsion integrals, but all one-center atomic exchange integrals are retained. This is the lowest level of sophistication that can be expected to include spin polarization in an interpretation of spin delocalization mechanisms in complex organic systems.

The wave functions obtained in this way are not eigenfunctions of the S^2 operator, but it has been shown that contributions from states of higher multiplicity make a negligible contribution to the isotropic hfsc.

The isotropic hfsc for a nucleus, N, is related to the wave function by

$$a_{\mathrm{N}} = (4\pi/3)g\beta\gamma_{\mathrm{N}}\hbar\langle S_z\rangle^{-1}\langle\psi|\rho(r_{\mathrm{N}})|\psi\rangle$$

where $\rho(r_{\mathrm{N}})$ is the spin density operator evaluated at the nucleus and is defined as

$$\rho(r_{\mathrm{N}}) = \sum_{k} 2S_{zk}\delta(r_k - r_{\mathrm{N}})$$

where r_k is the position vector for the kth electron, S_{zk} is the component of the electron spin angular momentum operator, and $\delta(r)$ is the Dirac δ function.

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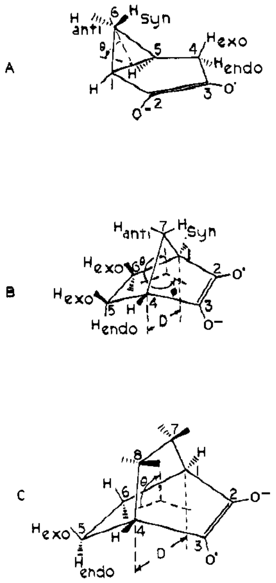

Figure 1. The structures and numbering of the bicyclic semidiones mentioned in this paper: (A) bicyclo[3.1.0]hexane 2,3-semidione; (B) bicyclo[2.2.1]heptane 2,3-semidione; (C) bicyclo[2.2.2]octane 2,3-semidione.

Thus the expectation value of the spin density operator becomes

$$\langle\psi|\rho(r_N)|\psi\rangle = \sum_{\mu\nu}\rho_{\mu\nu}\phi_\mu(r_N)\phi_\nu(r_N)$$

where

$$\rho_{\mu\nu} = P_{\mu\nu}^{\alpha} - P_{\mu\nu}^{\beta}$$

and the spin density matrices are defined by

$$P^{\alpha} = \sum_{i}^{a} c_{\mu i}{}^{\alpha} c_{\nu i}{}^{\alpha}$$

$$P^{\beta} = \sum_{i}^{b} c_{\mu i}{}^{\beta} c_{\nu i}{}^{\beta}$$

In order to simplify the evaluation of $\langle\psi|\rho(r_N)|\psi\rangle$ it is assumed that only those integrals for which ϕ_μ and ϕ_ν are centered on the same atoms make any significant contribution to the spin density of that atom. Since only the s orbital has nonzero density at the nucleus, the expectation value for the spin density operator reduces to

$$\langle\psi|\rho(r_N)|\psi\rangle = \rho_{s_N s_N}|\phi_{s_N}(r)_N|^2$$

where $\rho_{s_N s_N}$ is the unpaired electron density in the valence s orbital of atom N and $|\phi(r_N)|^2$ is the density of the s orbital at the nucleus. The quantity $|\phi(r_N)|^2$ may be evaluated empirically by recognizing a linear relation between a_N and $\rho_{s_N s_N}$ and using a least-squares analysis to obtain best agreement between theory and experiment. This method has been employed by Pople, *et al.*,[19] and we have used their proportionality constants in evaluating the carbon and oxygen hfsc's. Alternatively one could evaluate $|\phi_{s_N}(r_N)|^2$ directly.[21] We have chosen this method for the proton hfsc's, and in order to maintain consistency with our previous work[8] the evaluation was made using a Slater exponent of 1.20, a value which SCF calculations indicate to be most appropriate for simple hydrocarbons.[22] The exact value of $|\phi_{s_N}(r_N)|^2$ is of little consequence in this work, as it would result only in a change in the absolute magnitudes of the hfsc's. Since we are ultimately interested in evaluating the relative importance of the various spin delocalization mechanisms, we are most interested only in the signs and relative magnitudes of the hfsc's. As will be seen, this method does lead to quite acceptable agreement with experiment.

Geometries

The choice of appropriate geometries introduces a further degree of approximation into this study. While several precise studies of the geometry of bicyclic systems have been made,[23] no data are available for the corresponding semidiones nor for the relevant diketones. In principle one could obtain the most suitable geometry by minimizing the molecular energy with respect to $3N - 6$ internal coordinates, but the time and effort necessary for this would be prohibitive. We have thus used the previously discussed geometries,[8] which appear reasonable by comparison with known molecules, and, where doubt exists, we have varied the geometries to give an indication of the errors and trends involved. In all cases we have used the following bond lengths: C—C = 1.54 ± 0.03, CO—CO = 1.40, C=O = 1.22, and C—H = 1.09 Å. The H-C-H bond angles in $-CH_2-$ were assumed to be 111°, while for methine hydrogens all C-C-H angles at any particular carbon were made equal. The angle between the two C=O bonds was 70°.

The geometries and numbering of the relevant semidiones are shown in Figure 1, while the calculated hfsc's are compared with their most appropriate experimental counterparts in Table I. It should be noted that for most of the experimental values the limit of resolution is of the order of 0.1 G.[24]

Discussion

The agreement between the experimental and calculated values is quite encouraging considering the approximations which have been made. It therefore appears that the INDO-SCF method includes all major spin delocalization mechanisms without grossly overemphasizing any one of them.

In discussing the results we will use the following system of nomenclature

$$\begin{array}{cccc} C— & C_\alpha— & C_\beta— & C_\gamma \\ | & | & | & | \\ H_\alpha & H_\beta & H_\gamma & H_\delta \end{array}$$

According to conventional organic nomenclature, this system is strictly incorrect when applied to the semidiones (and most other radicals), but it is used here in deference to the popularly accepted format in epr literature.

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Table I. Observed and Calculated Hyperfine Splitting Constants for Semidiones

Bicyclo[3.1.0]hexane 2,3-Semidione

Position	1	4-exo	4-endo	5	6-anti	6-syn	^{17}O	$^{13}C_{CO}$	$^{13}C_\alpha$	$^{13}C_\beta$	$^{13}C_\beta$
Obsd[a]	4.0[b]	7.86	14.9	0.8	4.0	0.8					
Calcd[c]	1.57	4.80	11.13	−0.94	1.35	−0.19	8.23[d]	−1.35[d]	−1.60[d]	0.12[e]	1.49[f]
Calcd[g]	2.39	1.47	8.96	−0.99	3.31	−0.55	8.71[d]	−0.74[d]	−1.68[d]	0.61[e]	2.93[f]

6,6-Dimethylbicyclo[3.1.0]hexane 2,3-Semidione

Position	1	4-exo	4-endo	5	6-anti	6-syn	^{17}O	$^{13}C_{CO}$	$^{13}C_\alpha$	$^{13}C_\beta$	$^{13}C_\beta$
Obsd[a]	5.1	7.6	14.6	0.9	0.45[h]	0.0					
Calcd[c]	3.33	0.29	6.75	−0.98	0.28[i]	−0.15	8.81[d]	−0.87[d]	−1.82[d]	0.30[e]	2.56[f]

Bicyclo[2.2.1]heptane 2,3-Semidione

Position	1(4)	5(6)-exo	5(6)-endo	7-syn	7-anti	^{17}O	$^{13}C_{CO}$	$^{13}C_\alpha$	$^{13}C_\beta$	$^{13}C_\beta$
Obsd[j]	2.49	2.49	0.0	0.41	6.47					
Calcd[k]	1.74	1.69	−0.20	−0.56	7.55	8.49	−0.08	−1.78	3.42[l]	6.11[m]
Calcd[n]	1.71	3.50	−0.43	−1.06	12.98	8.40	0.05	−1.83	4.59[l]	10.84[m]
Calcd[o]	1.77	1.77	−0.19	−0.77	5.93	8.50	−0.10	−1.83	3.52[l]	6.02[m]
Calcd[p]	1.47	3.18	0.22	−0.44	7.99	8.40	0.07	−1.68	3.55[l]	5.76[m]

1-*syn*-7-Dimethylbicyclo[2.2.1]heptane 2,3-Semidione

Position	1(4)	5(6)-exo	5(6)-endo	7-syn	7-anti
Obsd[j]	0.2[h] (2.55)	2.55	0.0	0.2[h]	3.05

syn-7-Methylbicyclo[2.2.1]heptane 2,3-Semidione

Position	1(4)	5(6)-exo	5(6)-endo	7-syn	7-anti	^{17}O	$^{13}C_{CO}$	$^{13}C_\alpha$	$^{13}C_\beta$	$^{13}C_\beta$
Calcd	1.79[q]	1.72[q]	−0.15[q]	0.33[i]	4.40	8.48[q]	−0.07[q]	−1.87[q]	3.37[l,q]	5.96[m]

endo-5,6-Dimethylbicyclo[2.2.1]heptane 2,3-Semidione

Position	1(4)	5(6)-exo	5(6)-endo	7-syn	7-anti
Obsd[j]	2.33	1.84	0.2	0.4	6.97

endo-5-Methylbicyclo[2.2.1]heptane 2,3-Semidione

Position	1(4)	5(6)-exo	5(6)-endo	7-syn	7-anti	^{17}O	$^{13}C_{CO}$	$^{13}C_\alpha$	$^{13}C_\beta$	$^{13}C_\beta$
Calcd[o]	1.73 (1.78)	1.50 (1.48)	0.24 (−0.22)	−0.76	5.91	8.50[q]	−0.10[q]	−1.85[q]	3.63[q]	5.90[m]
Calcd[p]	1.44 (1.54)	2.99 (2.65)	0.34 (0.12)	−0.40	7.94	8.40[q]	−0.06[q]	−1.69[q]	3.65[q]	5.59[m]

Bicyclo[2.2.2]octane 2,3-Semidione

Position	1(4)	5,6,7,8-exo	5,6,7,8-endo	^{17}O	$^{13}C_{CO}$	$^{13}C_\alpha$	$^{13}C_\beta$
Obsd[j]	0.0	2.09	0.0				
Calcd[r]	−0.12	3.22	−0.27	8.56	0.09	−1.25	3.21
Calcd[s]	−0.11	5.42	0.14	8.43	0.27	−1.10	3.38
Calcd[t]	−0.02	3.41	−0.26	8.57	0.22	−1.36	3.18

endo-5,6-Dimethylbicyclo[2.2.2]octane 2,3-Semidione

Position	1(4)	5(6)-exo	7(8)-exo	5(6)-endo	7(8)-endo
Obsd[j]	0.0	1.34	2.12	0.0	0.0

endo-5-Methylbicyclo[2.2.2]octane 2,3-Semidione

Position	1(4)	5-exo	7(8)-exo	5-endo	7(8)-endo	^{17}O	$^{13}C_{CO}$	$^{13}C_\alpha$	$^{13}C_\beta$
Calcd	−0.11 (−0.13)	2.93	3.19[q]	0.18[i]	−0.26	8.56	0.10[d]	−1.27[q]	3.17[d]

1-Methyl-4-methoxybicyclo[2.2.2]octane 2,3-Semidione

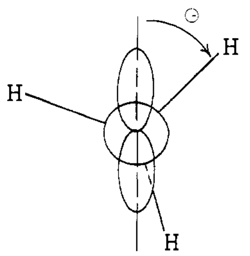
Position	1	6(7)-exo	6(7)-endo
Obsd[j]	0.0	2.14	0.0

1-Methylbicyclo[2.2.2]octane 2,3-Semidione

Position	1	6(7)-exo	6(7)-endo	^{17}O	$^{13}C_{CO}$	$^{13}C_\alpha$	$^{13}C_\beta$	$^{13}C_\beta$
Calcd	−0.19[i]	3.28	−0.29	8.58[d]	0.07[d]	−1.25[q]	3.16[d,l]	−0.02[u]

[a] Taken from ref 3c. [b] All values are in gauss. [c] See Figure 1, $\theta = 65°$. [d] Since the radical is unsymmetrical these are mean values only. [e] For β carbons in the ring most nearly planar with the carbonyl groups. [f] For carbon 6. [g] See Figure 1, $\theta = 75°$. [h] $a_{CH_3}{}^{H}$, three equivalent hydrogens observed. [i] Average value for three protons for one conformation only. [j] Taken from ref 28. [k] See Figure 1, $\theta = 128°$, $\phi = 110°$, $D = 2.286$ Å. [l] For the 5(6) carbon atoms. [m] For carbon 7. [n] See Figure 1, $\theta = 125°$, $\phi = 110°$, $D = 2.600$ Å. [o] See Figure 1, $\theta = 125°$, $\phi = 110°$, $D = 2.286$ Å. [p] See Figure 1, $\theta = 134°$, $\phi = 105°$, $D = 2.286$ Å. [q] Because only one conformation of the methyl group was considered, a slight asymmetry was introduced into the molecule. These hfsc's are therefore mean values. However the two values obtained differ from the mean by less than 5%. [r] See Figure 1, $\theta = 120°$, $D = 3.00$ Å [s] See Figure 1, $\theta = 130°$, $D = 3.00$ Å. [t] See Figure 1, $\theta = 120°$, $D = 3.20$ Å. [u] For the methyl carbon.

We shall discuss the results of our calculations in terms of the major spin delocalization mechanisms which have been considered in the literature. For β-proton hfsc's, the magnitude of the hyperconjugation interaction depends upon the degree of interaction of the electron in the carbonyl carbon $2p_z$ orbital with the electrons in the C_α–H_β σ bond, and therefore on the dihedral angle, θ. Thus as θ increases, the contribution to the hfsc from hyperconjugation decreases, whereas the contribution from spin polarization (spin transfer through σ bonds) should be independent of θ.



These effects are expressed in the $B \cos^2 \theta$ and B_0 terms, respectively, of the Heller–McConnell[25] expression

$$a_\beta^{H} = \rho(B_0 + B\cos^2\theta)$$

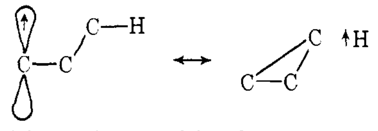
where $B_0 \ll B$.

It is seen that the 1-proton [β] hfsc's for the bicyclo[2.2.2]octane 2,3-semidiones are small and agree well with experiment. The dihedral angle here is 90° and consequently the hyperconjugation mechanism should make no contribution to the hfsc.

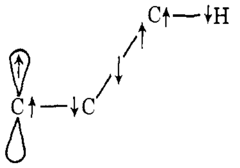
For the bicyclo[3.1.0]hexane 2,3-semidione, the calculated 4-exo-[β] and 4-endo-[β] proton hfsc's agree very well with experiment. The ratio of the calculated[26] hfsc's for these positions is 2.1:1.0 as compared with the experimental value of 2.0:1.0. Both of these protons have the same dihedral angle, but quite different hfsc's. This is not surprising considering their rigid, asymmetric environment, but could be viewed as a limitation to the Heller–McConnell equation, which has been so useful in conformational studies of free radicals,[27] in that the exo and endo protons would have to have different values of B and B_0.

The magnitude of the hfsc's for the γ protons listed in Table I are also in reasonable agreement with experiment. Note that the larger γ proton hfsc's are all positive. This result is in accord with the findings of extended-Hückel calculations[8] and is consistent with a homohyperconjugation mechanism which has been proposed by Russell.[28] However, this mechanistic interpretation is at variance with the experimental determinations of the signs of the hfsc's as performed by deBoer[9] and Kreilick,[10] who have found that in a large number of relatively flexible radicals, the γ-hydrogen hfsc's were negative. It should be noted that not all the γ-proton hfsc's in Table I are positive, nor are they all large, and that only those protons which obey the *W* rule[29] yield large positive hfsc's, *e.g.*, the 6-anti proton in bicyclo[3.1.0]hexane 2,3-semidione, the 5,6-exo and 7-anti protons in bicyclo[2.2.1]heptane 2,3-semidione, and the 5,6-exo protons in bicyclo[2.2.2]octane 2,3-semidione.

The change in sign for different types of γ protons suggests that a combination of two mechanisms is responsible for the proton hfsc. Homohyperconjugation, represented by

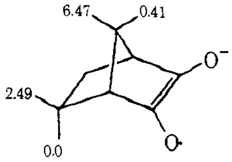


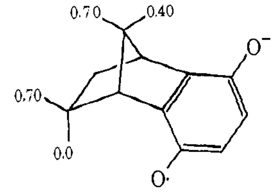
leads to positive spin densities for very specific geometries, while spin polarization, represented by

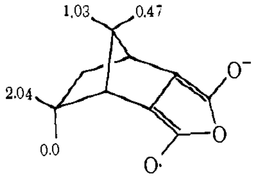


leads to (smaller) negative contributions to the spin densities. The spin polarization mechanism is expected to be operative over all conformations and consequently for those geometries not favorable to homohyperconjugation small or negative hfsc's could be anticipated, *e.g.*, the 5-endo proton in bicyclo[2.2.2]octane 2,3-semidione. Further experimental and theoretical evidence for this statement will be presented at a later date.

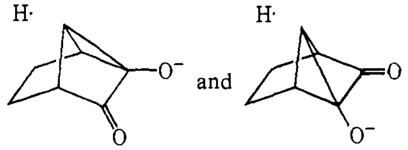
It is important to note, however, that the geometry and the spin density in the p_z orbitals are not the only factors which determine the magnitudes of the γ-hydrogen hfsc's. This is well illustrated by the magnitude of the hfsc's for the bicyclo[2.2.1]radicals in the semidione,[3a] semiquinone,[4b] and semifuraquinone[6a] series







The 7-anti proton hfsc is proportionally larger in the semidione than in either of the other radicals. This is particularly noticeable in a comparison of the semidione with the semifuraquinone where the γ-hydrogen hfsc's at the 5-exo, 5-endo, and 7-syn positions are of the same order of magnitude, but the 7-anti proton hfsc's differ by a factor of approximately 6. It is obviously not adequate to describe all the exo and the anti couplings in these radicals as being due to equal contributions from the same coupling mechanisms. Russell[30] and Stock[4b,31] and coworkers have pointed out that the singly occupied π orbital is symmetric in the semidiones but antisymmetric in both the semiquinones and semifuraquinones. Thus, in the latter two radicals there is a nodal plane for the highest singly occupied molecular orbital which coincides with the plane of molecular symmetry. This is borne out in the INDO calculations and it is necessary to infer that the two valence-bond structures of the form



make a proportionately larger contribution to the hfsc in the semidione than in either the semiquinone or the semifuraquinone. This is the result of molecular orbital symmetry enhancement (or reduction) of the homohyperconjugation mechanism. A similar situation pertains to the β-hydrogen interactions in the cyclobutenyl,[20a] cyclohexadienyl,[32] and cycloheptatriene

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(25) C. Heller and H. M. McConnell, *J. Chem. Phys.*, 32, 1535 (1960).

(26) Here we used the calculated values for a geometry with $\theta = 65°$ owing to analogy with other structures.[23a,d]

(27) (a) G. A. Russell, G. R. Underwood, and D. C. Lini, *J. Amer. Chem. Soc.*, **89**, 6636 (1967); (b) D. H. Geske, *Progr. Phys. Org. Chem.*, 4, 125 (1967).

(28) G. A. Russell, G. Holland, K.-Y. Chang, and L. H. Zalkow, *Tetrahedron Lett.*, 1955 (1967).

(29) See ref 3 and (a) J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, **83**, 2769 (1961); (b) C. W. Jefford, B. Waegell, and K. Ramey, *ibid.*, **87**, 2191 (1965); (c) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964), and references cited therein.

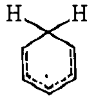
(30) G. A. Russell and P. R. Whittle, *J. Amer. Chem. Soc.*, **89**, 6781 (1967).

(31) K. E. Anderson, D. Kosman, C. J. Meyers, B. P. Reukberg, and L. M. Stock, *ibid.*, 90, 7168 (1968).

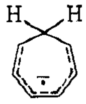
(32) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **38**, 773 (1963).

anion[33] radicals except that in these cases it is the hyperconjugation mechanism which is either enhanced or

4.45G



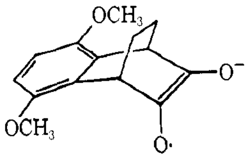
47.41G



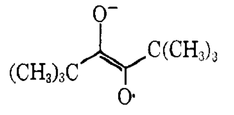
2.16G

reduced by the π molecular orbital symmetry. These results have been interpreted in a similar manner by Whiffen[34] and discussed most recently by Strom,[35] *et al.*

There have been few data reported for carbon-13 and oxygen-17 hfsc's in bicyclic systems.[36] The average value for the oxygen-17 coupling is calculated by us to be fairly constant at 8.5 ± 0.2 G. This compares well with 9.95 G reported for the carbonyl oxygen splitting in I,[36] which is the only *cis*-semidione for which the oxygen-17 hfsc has been determined.



I



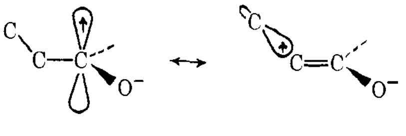
II

Only recently have experimental values for the ^{13}C hfsc's of semidiones become available.[37] Our calculated carbonyl carbon splittings are uniformly small and with just one exception are in the range −0.33 ± 0.54 G. These results are in accord with the absence of an observable carbon hfsc for the carbonyl carbons in I and II[36] and with the small values of the experimental $a_{\mathrm{CO}}{}^{\mathrm{C}}$ recorded for a variety of polycyclic semidiones.[37]

In the semidiones the α-carbon nuclei lie in the nodal plane of the p_z orbital, and, therefore, spin density at this nucleus would be expected to arise from a spin polarization mechanism. In accord with this expectation, the calculated $a_\alpha{}^{\mathrm{C}}$ values are all negative and are in the range −1.5 ± 0.4 G. These are substantially smaller than the experimental values of $a_\alpha{}^{\mathrm{C}}$ (4.5 ± 1.1 G[37]) for a variety of similar semidiones.

The relative constancy of the calculated carbonyl carbon, α-carbon, and oxygen hfsc's lends support to the assumption that the π spin density remains virtually unchanged in all the *cis*-semidiones.[14] The spin densities calculated for these radicals are $\rho_{\mathrm{CO}}{}^{\mathrm{C}} = 0.1$ and $\rho_{\mathrm{CO}}{}^{\mathrm{O}} = 0.4$. These values differ somewhat from $\rho^{\mathrm{O}} = \rho^{\mathrm{C}} = 0.25$, which is normally assumed,[14] and it is difficult at this stage for us to decide which is the more reliable set.

The β-carbon hfsc's appear to be very dependent upon geometry. In particular, we note that as the dihedral angle between the carbonyl p_z orbital and the C_α–C_β bond decreases, the value of $a_\beta{}^{\mathrm{C}}$ increases.[38] This trend also appears in the experimental values for similar systems.[37] This result suggests that the most important mechanism for spin delocalization to the β-carbon nucleus is carbon–carbon hyperconjugation.[39]



It should be pointed out that while the trend of our calculated carbon hfsc's follows that of the experimental values, the absolute magnitudes of the calculated values are smaller by a factor of 3. However, as mentioned earlier, there is considerable uncertainty in the value of $|\phi_{\mathrm{S_N}}(r_{\mathrm{N}})|^2$ which was determined empirically by Pople, *et al.*,[19] for a limited number of data. In view of the many recent experimental values for ^{13}C hfsc's, a redetermination of this parameter would seem appropriate.

Conclusion

The application of the INDO approximation of the SCF method yields satisfactory results for proton, carbon, and oxygen hfsc's in the rigid bicyclic semidiones and therefore appears to be suitable for use in the estimation of contributions from the various possible spin delocalization mechanisms. The results reported here indicate that γ-proton hfsc's result from several mechanisms but that the major contribution to the hfsc's of those hydrogens obeying the *W* rule is due to homohyperconjugation, which results in positive spin density at the proton. Those protons not obeying the *W* rule may have negative coupling constants and appear to result predominantly from a spin polarization mechanism transmitted through the σ framework. The calculated values of the α-carbon hfsc's are all negative, and therefore, in accord with a spin polarization mechanism. The β-carbon hfsc's, however, show contributions largely from carbon–carbon hyperconjugation.

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(34) D. H. Whiffen, *Mol. Phys.*, 6, 223 (1963).

(35) E. T. Strom, E. G. Janzen, and J. L. Gerlock, *ibid.*, in press.

(36) G. A. Russell and G. R. Underwood, *J. Phys. Chem.*, 72, 1074 (1968).

(37) G. A. Russell, D. F. Lawson, H. L. Malkus, and P. R. Whittle, unpublished results.

(38) G. R. Underwood, V. L. Vogel, and J. M. Iorio, unpublished results.

(39) C. Trapp, C. A. Tyson, and G. Giacometti, *J. Amer. Chem. Soc.*, 90, 1394 (1968).