Hyperconjugation and Through-Space and Through-Bond Interactions in Bridgehead Alkyl Radicals by Electron Spin Resonance

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Abstract: Solution ESR studies are reported for 1-norbornyl and bicyclo[2.1.1]hexan-1-yl radicals. The hyperconjugative spin transfer onto a β proton in a cis periplanar arrangement with the front lobe of the odd electron orbital decreases drastically as the geometry of the tervalent carbon atom becomes more pyramidal. The structural dependence of long-range odd electron delocalization is analyzed in terms of "through-space" and two modes of "through-bond" interactions. An important factor governing the magnitude of a long-range hyperfine splitting constant is shown to be the phase of the mixing of remote σ orbital(s) into the odd electron wave function.

There has been considerable recent interest in long-range interactions between remote orbitals. Hoffmann[1] and his co-workers examined this subject theoretically and devised the terminology of "through-space" and "through-bond" to distinguish the mode of the interaction. More or less following these concepts, long-range interactions have been studied by examining shifts of ionization potentials of lone pair or π orbitals,[2] contact shifts in NMR of amines induced upon complexation with Ni(II) ion,[3] and long-range couplings in NMR.[4]

Since the observation of long-range couplings in ESR spectra of bicyclo[2.2.1]heptane-2,3-semidiones by Russell and Chang,[5] long-range hyperfine interactions have been explored experimentally and theoretically.[6] However, mechanisms of long-range hyperfine interactions do not seem to be understood satisfactorily, and a new approach to this problem with concepts of "through-space" and "through-bond" interactions is expected to be fruitful. Some time ago Krusic, Rettig, and Schleyer[7] reported a pertinent ESR study on 1-adamantyl and bicyclo[2.2.2]octan-1-yl radicals. Bridgehead radicals of polycyclic compounds have unusually rigid structures and offer an opportunity to examine geometrical dependences of hyperconjugation and long-range interaction using ESR.[7-10] We report here an ESR study of the 1-norbornyl and the bicyclo[2.1.1]hexan-1-yl radicals and examine hyperconjugation between pyramidal radical centers and neighboring C–H bonds and effects of "through-space" and "through-bond" interactions on long-range couplings involved in 1-adamantyl (**1**),[7] bicyclo[2.2.2]octan-1-yl (**2**),[7] 1-norbornyl (**3**),[8a] and bicyclo[2.1.1]hexan-1-yl (**4**)[8b] radicals.
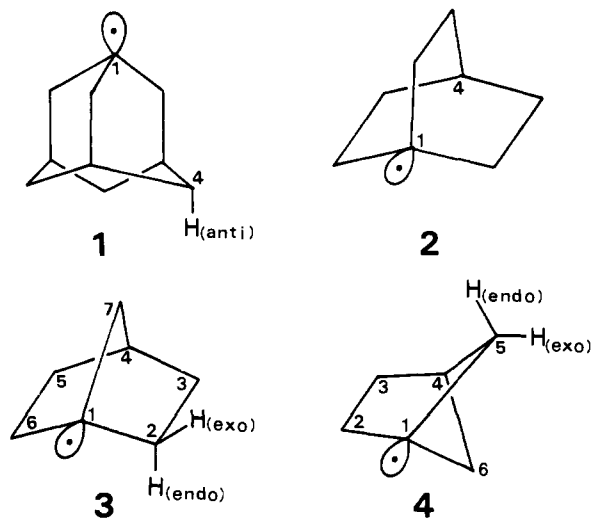
Results

Preparations. Radicals were photolytically generated from the corresponding diacyl peroxides, which were prepared by the treatment of the acid chlorides with sodium peroxide. Norbornane-1-carboxylic acid (**5**) was prepared according to a known procedure.[11] *exo-cis*-2,3-Dideuterionorbornane-1-carboxylic acid (**5x**) was obtained by deuteration of norbornene-1-carboxylic acid[12] with palladium–charcoal catalyst. *endo-cis*-2,3-Dideuterionorbornane-1-carboxylic acid (**5n**) was prepared as shown in Chart I. Bicyclo[2.1.1]hexane-1-
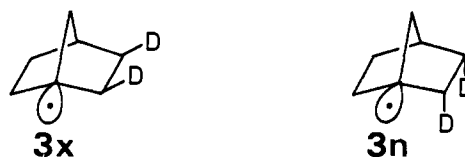
Chart I
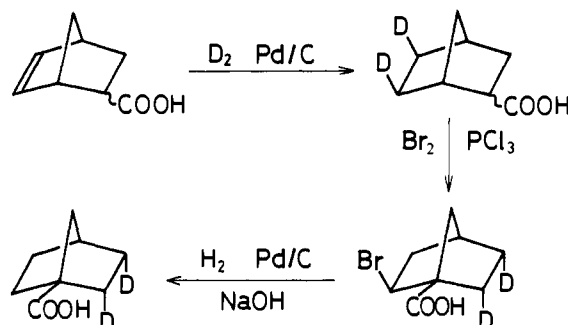
carboxylic acid[13] was prepared using a modification of the method of Liu and Hammond[14] (Chart II).

Chart II
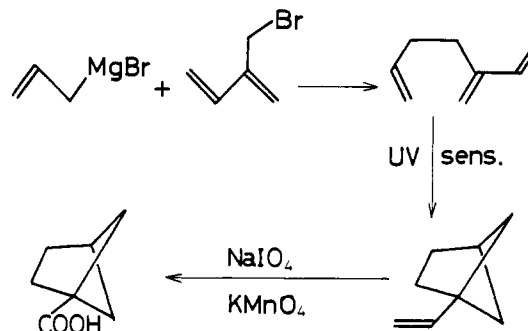
1-Norbornyl Radical (3). ESR spectra and their analyses of **3** and *exo-cis*-2,3-dideuterio-1-norbornyl radical (**3x**) have already been reported.[8a] The g factor[15] of **3** was 2.00258 at

1   2

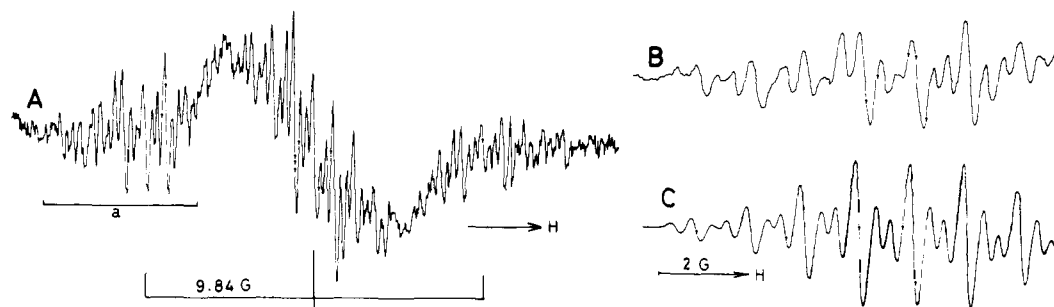3   4

3x   3n

Figure 1. (A) ESR spectrum of **3n**; (B) computer averaged spectrum of the underlined part a of the spectrum in A; (C) low-field wing of the simulated spectrum.
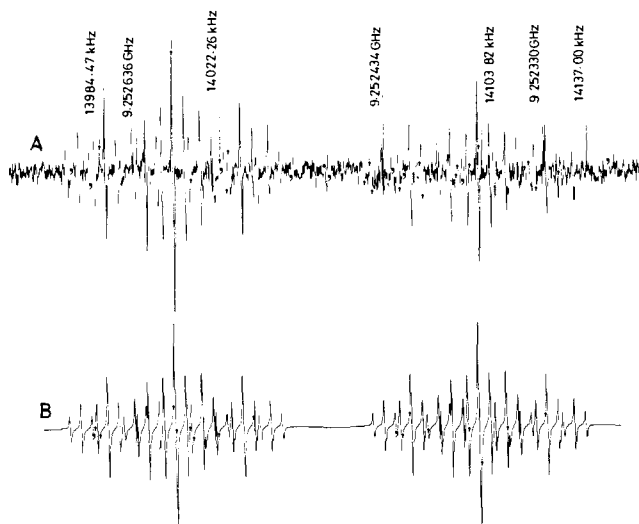

Figure 2. (A) The observed and (B) simulated spectrum of **4**. The number at markers in kHz and GHz units are ^{1}H NMR radio and ESR microwave frequencies, respectively.

Figure 3. The relation between the β-proton hfsc's and $\cos^2\theta$: ●, **1**; ○, **2**; ■, **3**; ▲, **4**.

−116 °C in liquid cyclopropane. The ESR spectrum of *endo-cis*-2,3-dideuterio-1-norbornyl radical (**3n**) was observed during photolysis of bis(*endo-cis*-2,3-dideuterionorbornane-1-carbonyl) peroxide in liquid cyclopropane at −122 °C (Figure 1). Table I summarizes the observed proton hfsc's of **3n** together with those of **3** and **3x**.[8a] The results in Table I clearly show the assignments of $a(H_4) = 2.45$ G and $a(H_7) = 2.35$ G for **3**. The triplets of 9.81 and 1.23 G of **3** arise from H_{2exo} and H_{3exo} and their equivalents. The best assignments are $a(H_{2exo}) = 9.81$ G and $a(H_{3exo}) = 1.23$ G on the basis of UHF-INDO[16] calculations.[8a] The remaining two sets of small triplet splittings are due to H_{2endo} and H_{3endo} and tentatively assigned as $a(H_{2endo}) = 0.49$ G and $a(H_{3endo}) = 0.36$ G.

Bicyclo[2.1.1]hexan-1-yl Radical (4). The spectrum of **4** was observed during photolysis of a cyclopropane solution of bis-(bicyclo[2.1.1]hexane-1-carbonyl) peroxide at −116 °C (Figure 2). The spectrum consisted of a doublet (22.49 G) and three sets of triplets (5.01, 2.01, and 0.84 G) with a *g* factor

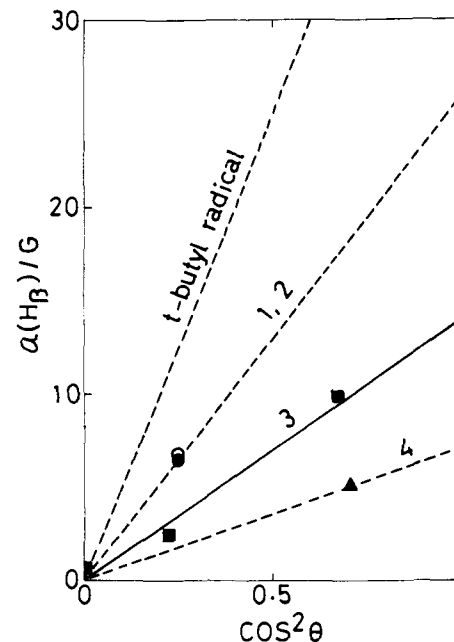of 2.00257. The assignment of the doublet of 22.49 G to the bridgehead proton, H_4, is straightforward from the molecular symmetry of this radical. UHF-INDO calculations of this radical showed that the hfsc of H_{5exo} is fairly large (3-6 G) in comparison to those of H_2, H_3, and H_{5endo} (0.5-2.3 G).[8b] On this basis the triplet of 5.01 G is assigned to H_{5exo}.

Discussion

Hyperconjugation. The β-proton hfsc is well established as originating from hyperconjugation.[17,18] A proton hfsc of a methyl group bonded to a pyramidal tervalent carbon atom is smaller than that bonded to a planar center.[19] However, the geometrical dependence of hyperconjugation between an odd electron orbital on a pyramidal center and a neighboring

Table I. Observed Hfsc's of **3**, **3x**, and **3n**[a]

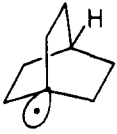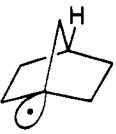| Radical			Hfsc's, G			
3	9.81 (2 H)	2.45 (1 H)	2.35 (2 H)	1.23 (2 H)	0.49 (2 H)	0.36 (2 H)
3x	9.88 (1 H)	2.53 (1 H)	2.38 (2 H)	1.23 (1 H)	0.53 (2 H)	0.34 (2 H)
	1.50 (1 D)			0.17 (1 D)		
3n	9.84 (2 H)	2.39 (1 H)	2.39 (2 H)	1.22 (2 H)	0.46 (1 H)	0.46 (1 H)
					b	*b*
Assignt	H_{2exo}	H_4	H_7	H_{3exo}	H_{2endo}	H_{3endo}

[a] A note in parentheses designates the nucleus and the number of the equivalent nuclei. [b] The splitting due to the deuterium nucleus was less than the line width (0.25 G).

C_β–H_β bond is still not clear; the present radicals are relevant for a study of this dependence.

In Figure 3 β-proton hfsc's of bridgehead radicals are plotted against values of $\cos^2 \theta$, where θ are dihedral angles between the odd electron orbitals on radical centers and the C_β–H_β bonds. The dihedral angles are approximated by those between the bridgehead C_1–H_1 bonds and the neighboring C–H bonds in the parent molecules.[20] The plots for **3** fit fairly well the equation of $a(H_\beta) = B\rho \cos^2 \theta$, where $B\rho \simeq 14$ G. If β-proton hfsc's of **1, 2,** and **4** are assumed similarly proportional to $\cos^2 \theta$, values of $B\sigma$ for **1** and **2** are estimated as 26 G, and for **4** as 7 G. The corresponding value for the more planar *tert*-butyl radical[21] is estimated as around 45 G.[22] The spin densities, ρ, on the radical centers of these radicals are calculated to be in the range of 0.8–0.95 with the UHF–INDO method. The dramatic change on the values of $B\rho$ of the present species are thus due to shifts in the constant B. It should be pointed out that all the C_β–H_β bonds in the present bridgehead radicals occupy cisoidal positions relative to the sp^n hybridized odd electron orbitals on the radical centers. Thus it is concluded that the hyperconjugative spin transfer from the odd electron orbital on a pyramidal center onto a cis periplanar C_β–H_β bond decreases drastically as the geometry of the radical center becomes more pyramidal. This is in parallel with the conclusion obtained by Bingham and Schleyer[23] from the analysis of bridgehead reactivities that cis periplanar C_β–H (or C_β–C_γ) bonds (relative to the leaving group) do not exert much hyperconjugative stabilization on the developing cationic center.
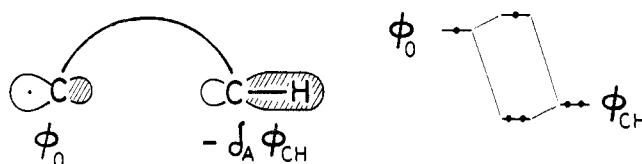
"Through-Space" and "Through-Bond" Interactions. The most interesting point in the present radicals occurs in the unexpected structural dependence of the hfsc's of the bridgehead protons of **2, 3,** and **4.** As the chain length of C–C bonds connecting the bridgehead carbon atoms decreases from **2** to **3** and to **4,** the bridgehead proton hfsc decreases slightly from 2.69 G[7] to 2.45 G followed by a drastic increase to 22.49 G. Chart III summarizes the bridgehead proton hfsc's together

Chart III

2·69 G[7]	2·45 G	22.49 G
2·59 Å[20c]	2·32 Å[20a]	2·17 Å[20b]
130°	125°[20a]	170°[20b]

with the distances between the bridgehead carbon atoms and the angles between two bridgehead C–H bonds in the parent alkanes, which are fair sources from which to estimate the geometrical arrangement of the bridgehead C–H bonds and the odd electron orbitals on the opposite sites. The data in Chart III show that the bridgehead proton hfsc is not only a function of the geometrical arrangement but also possibly a function of the length of the C–C bond chain connecting the bridgehead carbon atoms. This becomes more clear through UHF–INDO calculations. When the "through-space" interactions between the bridgehead carbon atoms are artificially removed,[24] the calculated bridgehead proton hfsc of **2** increases from 2.3 G to 7.1 G, whereas those of **3** and **4** decrease from 3.6 G to 1.1 G and from 21.4 G to 10.4 G, respectively. Here we examine effects of "through-space" and "through-bond" interactions on long-range hfsc's to interpret these interesting structural dependence of the bridgehead proton couplings.

First, we examine the odd electron delocalization onto a remote C–H bond by the "through-space" mechanism. The


C–H σ bonding orbital (ϕ_{CH}) mixes out-of-phase into the odd electron orbital (ϕ_0) by the "through-space" interaction (i.e., $\langle \phi_{CH}|H|\phi_0 \rangle$). This is expressed as

$$\phi_0' = \phi_0 - \delta_A \phi_{CH} \tag{1}$$

where δ_A is a small positive number,[25] and H designates the long-range interaction Hamiltonian.

Second, we consider the "through-bond" interaction between two carbon atoms connected with three C–C σ bonds. We designate it "through-three-bond" interaction, which is operative when the particular orbitals on the terminal atoms and the central C–C bond in the connecting methylene chain are periparallel. The σ bonding orbital of the central C–C bond (ϕ_{CC}) mixes out-of-phase into the odd electron orbital by the matrix element of $\langle \phi_{CC}|H|\phi_0 \rangle$, resulting in a delocalized odd electron orbital of $\phi_0 - \delta_B \phi_{CC}$, where δ_B is positive.[26] Into this
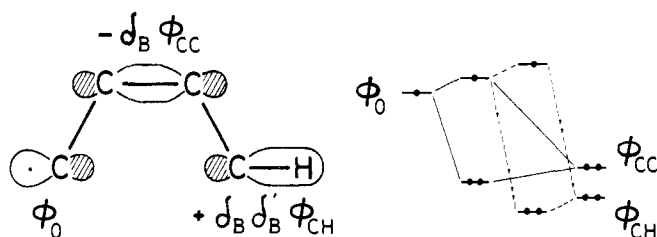
delocalized orbital, the matrix element of $\langle \phi_{CH}|H|\phi_{CC} \rangle$ mixes the terminal C–H σ bonding orbital (ϕ_{CH}) in an out-of-phase manner in the interacting region. This is expressed as

$$\phi_0' = \phi_0 - \delta_B \phi_{CC} + \delta_B \delta_B' \phi_{CH} \tag{2}$$

where δ_B' is also positive.[26] As a result of this "through-three-bond" interaction ϕ_{CH} is indirectly mixed in-phase into ϕ_0.

Third, we examine the "through-bond" interaction between the terminal atoms connected with two C–C σ bonds in a periplanar W plan arrangement. In this case the relay orbital is a linear combination of the two C–C σ bonding orbitals antisymmetric to the bisector of the C–C–C angle.[27] This relay orbital is designated as ϕ_C. The relay orbital ϕ_C mixes out-of-phase into ϕ_0. The interaction matrix element of $\langle \phi_{CH}|H|\phi_C \rangle$ mixes ϕ_{CH} into ϕ_0 through ϕ_C as expressed in

$$\phi_0' = \phi_0 - \delta_C \phi_C - \delta_C \delta_C' \phi_{CH} \tag{3}$$

where δ_C and δ_C' are small positive numbers.[26] This mode of interaction, "through-two-bond" interaction, has induced an
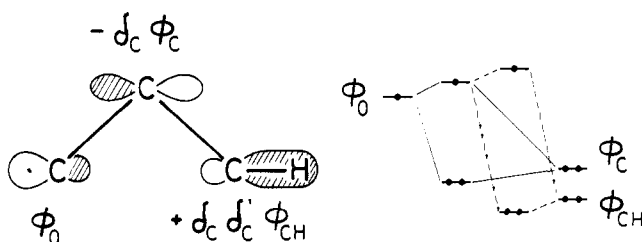
indirect out-of-phase mixing of ϕ_{CH} into ϕ_0.

When these "through-space," "through-three-bond", and "through-two-bond" interactions are operative, the delocalized odd electron orbital is expressed as

$$\phi_0' = \phi_0 - (\delta_A - n_B \delta_B \delta_B' + n_C \delta_C \delta_C')\phi_{CH} + \ldots \tag{4}$$

Table II. Analysis of Long-Range Proton Hfsc's by Equation 5

Radical Proton	1 H_{4anti}	2 H_4	3 H_4	4 H_4
A^a	0.09	1.15	0.87	1.41
B^a	0.92^b	0.92	0.92	0.92
C^a	c	c	2.13	2.13^b
n_B	2	3	2	1
n_C	0	0	1	2
a_H, calcd^d	3.06	2.59	1.35	22.6
a_H, exptl^d	3.08^e	2.69^e	2.45^f	22.49^f

^{a} In unit of $G^{1/2}$. ^{b} This is evaluated so as to fit the calculated a_H to the experimental one and applied to other radicals as a constant. ^{c} Not applicable. ^{d} In unit of G. ^{e} Reference 7. ^{f} Present result.

where n_B and n_C are the number of paths of the "through-three-bond" and "through-two-bond" interactions, respectively. The hfsc of the proton (a_H) is proportional to the odd electron density on the C–H bond, namely, the square of the coefficient of ϕ_{CH} in eq 4. This relation is given as

$$a_H = (A - n_B B + n_C C)^2 \quad (5)$$

where A, B, and C are due to the "through-space", "through-three-bond", and "through-two-bond" interactions, respectively, and always have the same sign (positive sign is adopted here).

The interesting point of eq 5 is that the "through-three-bond" interaction counteracts the "through-space" and "through-two-bond" interactions in delocalizing the odd electron onto the C–H bond, whereas the latter two interactions are cooperative in the odd electron delocalization. This "phase effect" is quite similar to the results obtained in theoretical and experimental studies[28] of ionization potentials of lone pairs of 1,4-diazabicyclo[2.2.2]octane, namely, the energy level of the symmetric combination of the localized lone pair orbitals is shifted upward by the "through-bond" ("through-three-bond" in the present terminology) interaction and downward by the "through-space" interaction.

Now we proceed to numerical estimates of A, B, and C and examine the validity of eq 5. The contribution of the "through-space" mechanism, A, is evaluated by UHF–INDO calculations. The bridgehead proton hfsc's were calculated including (i.e., normal calculations) and excluding the "through-space" interaction between the bridgehead carbon atoms. The comparison of these calculated hfsc's in accordance with eq 5 gave A values listed in Table II.

Both "through-two-bond" and "through-three-bond" interactions are successive double hyperconjugation. Therefore values of B and C are functions of geometrical arrangements of the odd electron orbital, the relay, and the C–H σ orbitals and also depend on hybridization (degree of planarity) of the radical center. However, B and C for long-range hfsc's of the present work are expected to be distributed in rather narrower ranges of values than A values. We thus tentatively assume B and C as constant, ignoring the dependence of B and C on the geometrical arrangements of orbitals and on the degree of the planarity of radical centers. The value of B was estimated as 0.92 $G^{1/2}$ to reproduce the experimental $a(H_{4anti})$ of **1**. When the value of C is assumed to be 2.13 $G^{1/2}$, the calculated value of $a(H_4)$ of **4** coincides with the observed one. With thus evaluated values of A, B, and C, eq 5 reproduces the bridgehead proton hfsc's of **2** and **3** fairly well (Table II), which demonstrates the validity of eq 5.

The results in Table II show that the curious structural dependence of the bridgehead proton hfsc's is arising from the "phase effect" in the odd electron delocalization by "through-space," "through-three-bond", and "through-two-bond" mechanisms. The odd electron density on H_{4anti} of **1** is

practically due to the double "through-three-bond" interactions. The odd electron is delocalized onto H_4 of **2** mainly by the triple "through-three-bond" mechanisms as suggested by Krusic, Rettig, and Schleyer,[7] but partly canceled by the "through-space" interaction. In **3**, both the single "through-two bond" and the "through-space" interactions are dominant in delocalizing the odd electron onto H_4 but the double "through-three-bond" interactions partly counteract them. Thus bridgehead proton hfsc's of **2** and **3** are rather small. The odd electron delocalization onto the bridgehead hydrogen atom of **4** is mainly due to the "through-space" and the double "through-two-bond" mechanisms, and the single "through-three-bond" interactions cancels out this delocalization to only a small extent.

As an extension of the analysis in Table II, eq 5 suggests that the bridgehead proton of bicyclo[1.1.1]pentan-1-yl radical (**6**) may have one of the largest γ-proton hfsc's possible for alkyl radicals. The value of A is estimated as 1.81 $G^{1/2}$ by UHF–INDO calculations. Thus the present treatment of the long-range interactions predicts 67 G for the bridgehead proton hfsc of this radical. In parallel to this estimation, the correlation between long-range couplings in ESR and NMR also predicted this γ-proton hfsc to be around 60 G.[29] These estimations can be expressed as a resonance between **6** and **7** with a fairly large contribution of the valence bond structure of **7**.

6   **7**
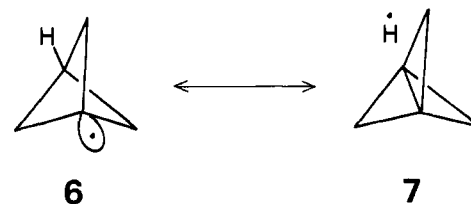
The present analysis shows that a large hfsc of a γ proton in a periplanar W plan arrangement with respect to the odd electron orbital is originating from the cooperative "through-space" and "through-two-bond" interactions and that extra ethano bridge(s) between the α and γ carbon atoms decreases the long-range coupling by the "through-three-bond" interaction through the "phase effect". This is well exemplified also in the following examples. The 6-exo proton of the 2-norbornyl radical (**8**) has a long-range coupling of 9.0 G,[30]

8   **9**
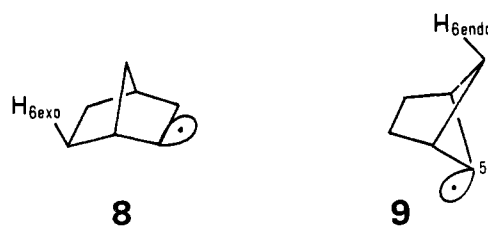
which is far larger than the bridgehead proton hfsc of **3** (2.45 G) although the latter has a rigid planar W plan arrangement. This is due to the absence of extra ethano bridges between the α and γ carbon atoms in the former. The 6-endo proton of the bicyclo[2.1.1]hexan-5-yl radical (**9**) is arranged in a double periplanar W plan relative to the odd electron orbital, and has a large coupling of 28.2 G.[31] The bridgehead proton of **4** is practically equivalent (with respect to long-range interactions) to the 6-endo proton of **9** but with an extra ethano bridge between C_5 and C_6. The hfsc of the bridgehead proton of **4** is, therefore, smaller than that of H_{6endo} of **9**.

Experimental Section

General Comments. ^{1}H NMR spectra were obtained at 220 and 60 MHz by using a Varian HR-220 spectrometer and a JEOL PMX-60 spectrometer, respectively. PFT ^{13}C NMR spectra were taken on a JEOL PFT-100 spectrometer operating at 25.1 MHz. Tetramethylsilane was used as internal standard and $CDCl_3$ as solvent for all the

NMR measurements. Infrared (IR) spectra were determined on a Hitachi 215 spectrometer. Mass spectra (MS) were obtained by using a JEOL JMS-01SG spectrometer.

ESR Measurements. ESR spectra were observed on a JEOL PE-2X spectrometer modified with a JEOL ES-SCXA gunn diode microwave oscillator unit or on a JEOL PE-1X spectrometer with a cylindrical mode cavity with slits for UV irradiation. Photolysis was performed with a Philips SP-500 super high pressure mercury lamp focused with two quartz lenses and filtered by a distilled water cell of 45 mm path length. Computer averaging of ESR spectra and simulations were performed on JEOL RA-1 or JEC-6 minicomputers.

exo-cis-2,3-Dideuterionorbornane-1-carboxylic Acid (5x). A solution of 0.90 g (6.5 mmol) of norbornene-1-carboxylic acid[12] in 50 mL of ethyl acetate was deuterated under deuterium gas at atmospheric pressure in the presence of 0.1 g of 5% palladium–charcoal catalyst and 1.5 mL of D_2O. The absorption of deuterium gas was complete in 15 min. After removal of the catalyst by filtration the acid was extracted with 0.3 N NaOH aqueous solution. The aqueous extract was washed with ether and acidified with concentrated HCl and the precipitate was recrystallized from *n*-pentane to give 0.70 g (77%) of the deuterated acid, 5x: MS *m/e* (rel intensity) 143 (9), 142 (100), 141 (6), 140 (0.5).

endo-cis-2,3-Dideuterionorbornane-1-carboxylic Acid (5n). A mixture of 5-norbornene-2-*exo*-carboxylic and 5-norbornene-2-*endo*-carboxylic acids was deuterated at atmospheric pressure with palladium–charcoal catalyst. The deuterated mixture was treated with bromine in the presence of a small amount of phosphorus trichloride[11] to give 2-*exo*-bromo-*endo-cis*-5,6-dideuterionorbornane-1-carboxylic acid. Dehalogenation of this acid was carried out by hydrogenation at atmospheric pressure of 2.0 g (9.0 mmol) of this bromo acid in 20 mL of methanol–water (3:1 by volume) containing 1.2 g of NaOH and 0.5 g of 5% palladium–charcoal.[32] Purification by sublimation (100 °C at 7 mmHg) followed by recrystallization from *n*-hexane gave 0.9 g (70%) of *endo-cis*-2,3-dideuterionorbornane-1-carboxylic acid: MS *m/e* (rel intensity) 143 (9), 142 (100), 141 (23), 140 (1.4).

Stereochemistry of Deuterium Atoms of 5x and 5n. ^1H NMR spectra (220 MHz) of 15 mg of 5, 5x, or 5n dissolved in about 0.4 mL of $CDCl_3$ were examined with additions of 2–5-mg portions of predried tris(heptafluorobutanoylpivaloylmethanato)europium (Eu-fod). The analysis of these spectra gave the following ^1H NMR parameters for 5. Relative paramagnetic low-field shifts: H_{2exo} (100), H_{2endo} (82), H_{3exo} (40), H_{3endo} (39), H_4 (34), H_7 (85). Chemical shifts in the absence of Eu-fod: H_{2exo} (δ 1.90), H_{2endo} (δ 1.59), H_{3exo} (δ 1.66), H_{3endo} (δ 1.33), H_4 (δ 2.32), H_7 (δ 1.60). Couplings in unit of Hz: $J(H_{2exo}, H_{2endo}) \simeq J(H_{3exo}, H_{3endo}) \simeq J(H_{2exo}, H_{3exo}) \simeq 12$, $J(H_{2endo}, H_{3endo}) \simeq 9$, $J(H_{2endo}, H_{3exo}) \simeq J(H_{3exo}, H_4) \simeq 4.5$, $J(H_{2exo}, H_{3endo}) \simeq 4$. When 16 mg of Eu-fod was added to the sample, most of the signals were separated as H_{3endo} (δ 1.8), H_{3exo} (δ 2.1), H_{2endo} and H_7 (δ 2.5–2.6), H_4 (δ 2.7), and H_{2exo} (δ 3.0), and the examined area of the peaks confirmed the stereochemistry of deuterium atoms of 5x and 5n.

3-Methylene-1,6-heptadiene. To a stirred solution of 29 g (0.20 mol) of 2-bromomethyl-1,3-butadiene[33] in 180 mL of absolute ether was added dropwise 300 mL of 0.90 mol/L ethereal solution of allylmagnesium bromide (0.27 mol) keeping the reaction temperature around 5 °C. After the addition the reaction mixture was stirred for 0.5 h at room temperature and 80 mL of saturated NH_4Cl aqueous solution was added. After removal of precipitates by filtration the organic layer was washed with water, dried over $CaCl_2$, and concentrated to about 100 mL on a rotary evaporator. After removal of the remaining solvent by fractional distillation at atmospheric pressure in the presence of hydroquinone, fractional distillation with a short Vigreux column under reduced pressure gave 11 g (51%) of 3-methylene-1,6-heptadiene (bp 45–62 °C at 67 mmHg) and 2.5 g (20%) of 3,6-dimethylene-1,7-octadiene (bp 87–96 °C at 67 mmHg). Spectral data of 3-methylene-1,6-heptadiene: IR (liquid film) 3080, 2980, 2950, 1595, 985, 910–885 cm^{-1}; ^1H NMR (60 MHz) a complex group of peaks around δ 2.2$_7$ (4 H), a complex group of peaks between δ 4.8$_0$ and δ5.4$_3$ (6 H), a double doublet (11 and 17 Hz) centered at δ 6.3$_2$ (1 H); proton decoupled ^{13}C NMR δ 30.6, 32.1, 112.8, 114.0, 115.6, 137.9, 138.7, 145.3. Spectral data for 3,6-dimethylene-1,7-octadiene: IR (liquid film) 3080, 2980, 2940, 1590, 985, 910–885 cm^{-1}; ^1H NMR (60 MHz) a sharp singlet at δ 2.3$_6$ (4 H), a complex group of signals between δ 4.8$_3$ and δ 5.3$_2$ (8 H), a double doublet (11 and 17 Hz) at δ 6.3$_2$ (2 H); proton decoupled ^{13}C NMR δ 30.0, 112.8, 115.6, 138.6, 145.7.

Bicyclo[2.1.1]hexane-1-carboxylic Acid. Photochemical cyclization of 3-methylene-1,6-heptadiene sensitized by β-acetonaphthone gave 1-vinylbicyclo[2.1.1]hexane.[14] A solution of 16 g (75 mmol) of NaIO$_4$ and 0.2 g of KMnO$_4$ in 350 mL of water was added dropwise during 2 h to a stirred suspension of 1.0 g (9.2 mmol) of 1-vinylbicyclo[2.1.1]hexane and 13 g of $Na_2CO_3 \cdot H_2O$ in 300 mL of *tert*-butyl alcohol–water (1:2 by volume) at room temperature. After removal of precipitates by filtration and addition of 0.5 g of NaOH, the aqueous solution was washed with ether, acidified with concentrated HCl, and extracted with ether. The ether extract was washed with water and dried over anhydrous $MgSO_4$ and the ether was evaporated. The residual viscous oil was sublimed (100 °C at 20 mmHg) giving 0.7 g (60%) of bicyclo[2.1.1]hexane-1-carboxylic acid.

Diacyl Peroxides.[34] A carboxylic acid was treated with thionyl chloride to give an acid chloride. The acid chloride was reacted with sodium peroxide in ether in the presence of a few drops of water to give the corresponding diacyl peroxide.[35] In a typical run, 0.25 g (1.7 mmol) of bicyclo[2.1.1]hexane-1-carbonyl chloride, 85 mg (1.1 mmol) of sodium peroxide, and 2 drops of water in 20 mL of ether were stirred for 24 h in an ice–water bath. Water (15 mL) was added and stirred for a few minutes and the ether layer was separated and stirred magnetically with $NaHCO_3$ aqueous solution in an ice–water bath for 1 h. The ether layer was washed with cold water and dried over anhydrous $MgSO_4$. Removal of ether by nitrogen gas flow (no applied heat) gave white, crystalline bis(bicyclo[2.1.1]hexane-1-carbonyl) peroxide: IR (CCl_4) 1795, 1770 cm^{-1}. Peroxides were stored as a *n*-pentane solution (or suspension) in a freezer.

A trial to prepare bis(5,5-dimethylbicyclo[2.1.1]hexane-1-carbonyl) peroxide similarly from the corresponding acid chloride was, however, unsuccessful.

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Carbon-13 Spin–Lattice Relaxation and Molecular Motion of Diphenyl Dichalcogenides

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Abstract: Spin-lattice relaxation times (T_1) were measured and analyzed for Ph_2X_2 type molecules (X = S, Se, Te), to obtain information on the relative order of magnitude of internal motion rates, which are otherwise inaccessible. The calculations were based on the rigid anisotropic as well as on the isotropic with internal rotation model of reorientation. Both the approaches suggested an interpretation of T_1 data in terms of intramolecular motions that contribute to relaxation at a rate increasing in the order S, Se, Te. In particular, the analyses provided evidence that for Ph_2Se_2 and Ph_2Te_2 the internal motion is much faster than in the Ph_2S_2 molecule, where conformational motions about Ph–S bonds occur at a rate that is comparable to that of overall molecular reorientation.

Introduction

The static stereochemistry of diphenyl disulfide and its selenium and tellurium analogues in the solution state has been the object of previous dipole moment and NMR studies.[2-5] Speculation concerning the origin and the temperature effect of the electrical dipole moments of these molecules recently[5] suggested peculiar variable internal flexibility along the series S, Se, Te. No direct and more detailed information, however, can be attained by conventional NMR techniques as to the motional characteristics of these systems.

Carbon-13 spin–lattice relaxation times are becoming an increasingly powerful tool for studies on internal motions as well as overall molecular tumbling characteristics.[6] The quantitative treatment of relaxation data, which is possible in that the majority of ^{13}C nuclei in organic molecules are relaxed by the dipole–dipole mechanism,[6-8] implies in general a fitting procedure with an appropriate relaxation model. Furthermore, the quantitative description of dipolar relaxation becomes complex when the nuclei are part of a group within the molecule that undergoes internal motion and, in particular, when more than one degree of freedom for internal motion is involved. Owing to these difficulties, the molecules investigated in some detail were mostly chosen for methodological demonstration purposes and not for their intrinsic chemical interest. Previous carbon-13 T_1 studies of structurally simple molecules bearing phenyl groups are reported[9-13] in the literature; these

were instrumental in interpreting the relaxation data in terms of overall anisotropic motion.

A detailed study of the spin–lattice relaxation behavior of diphenyl disulfide (Ph_2S_2), diphenyl diselenide (Ph_2Se_2), and diphenyl ditelluride (Ph_2Te_2) is therefore reported here. The determination of relaxation information for these diphenyl dichalcogenides offered, in fact, an opportunity to apply the method to more complex systems and, at the same time, to gain an insight into their dynamic conformational processes. The present study was thus initiated to provide unequivocal evidence for stereochemical nonrigidity of diphenyl dichalcogenides and to ascertain whether information on the relative order of magnitude of internal molecular motion along the series S, Se, Te could be derived from relaxation times.

Experimental Section

The peak assignments and ^{13}C spin–lattice relaxation times of the compounds studied have been reported in a previous work.[14] Experimental conditions and sources of materials have been described therein.

The proton noise-decoupled ^{13}C spectrum of each compound was recorded under nonsaturating conditions and all protonated carbon nuclei signals were found to have equal integral peak areas. This indicates that the relaxation is dipolar and the conditions for motional narrowing are satisfied.

All samples were carefully degassed prior to experiments.