Electron Spin Resonance Study of the Pyramidal Geometry around the Tervalent Carbon Atom of the Bicyclo[2.1.1]hexan-5-yl Radical[1)]

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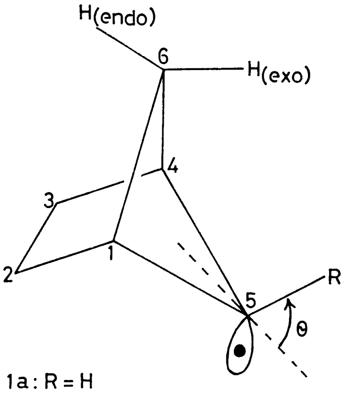
The bicyclo[2.1.1]hexan-5-yl and the 5-deuteriobicyclo[2.1.1]hexan-5-yl radicals have been examined using ESR. A comparison of the spectra confirmed that geometry around C_5 is pyramidal and showed highly stereoselective long-range spin-transfer from C_5 to the endo proton on C_6; $a(H_{6endo})=28.22$ and $a(H_{6exo})=0.49$ G. A potential curve for the out-of-plane bending motion of the C_5–H_5 bond, selected from the trial curves gave a reasonable simulation of the temperature dependence and isotope effects on $a(H_5)$ and $a(H_{6endo})$. The curve has two minima with a relatively low barrier to inversion; the geometry of the C_5–H_5 bond bent in the exo direciton has been estimated as approximately 0.9 kcal/mol more stable than that with the C_5–H_5 bond located in the endo direction.

Stereospecific intramolecular interactions in bicyclo[2.1.1]hexanes have been of theoretical and experimental interest for several years and large long-range nuclear spin couplings between the two endo protons on methano bridges of bicyclo[2.1.1]hexanes have been observed.[2)] A strong interaction has been revealed by the nonempirical molecular orbital calculation of bicyclo[2.1.1]hexane between the two endo C–H bonds on the methano bridges.[3)] Furthermore the *endo*-bicyclo[2.1.1]hexan-5-yl tosylate has been found to undergo faster solvolysis, by a factor of 10^8 than the exo isomer.[4)] All these results indicate a strong stereospecific intramolecular interaction operating between the two endo C–H bonds on the methano bridges.



1a: R = H
1b: R = D

The potential curves for the umbrella-mode vibrations around tervalent carbon atoms of several alkyl radicals have been correlated with the temperature dependence and the isotope shifts of hyperfine splitting constants (hfsc) of α carbon nuclei and/or α protons.[5)] In the bicyclo[2.1.1]hexan-5-yl radical (**1a**), the temperature dependences of $a(H_5)$ and $a(H_{6endo})$ and their shifts upon replacement of H_5 with a deuterium atom are closely correlated with the out-of-plane bending motion of the C_5–H_5 bond.[1b)] The potential curve for this motion will be estimated by simulating the temperature dependence and isotope effects with the aid of geometrical dependence of spin distribution calculated from INDO-UHF method.[6)]

Results and Discussion

*ESR Spectra and Stable Geometry of **1**.* The radical **1a** and the 5-deuteriobicyclo[2.1.1]hexan-5-yl radical, **1b**, have been generated in an ESR cavity by the photolysis of bis(bicyclo[2.1.1]hexane-5-carbonyl) peroxide and bis(5-deuteriobicyclo[2.1.1]hexane-5-carbonyl) peroxide in cyclopropane solvent, respectively. Typical ESR spectra for these radicals and the computer simulations have been published elsewhere.[1)] The spectrum of **1a** at −115 °C has been analyzed as three sets of doublets (28.22, 9.14, and 0.49 G), split further into three sets of 1 : 2 : 1 triplets (0.80, 0.49, and 0.25 G) with a g factor of 2.0027_6. At the same temperature the spectrum of **1b** consisted of two sets of doublets (28.80 and 0.50 G), three sets of 1 : 2 : 1 triplets (0.82, 0.36, and 0.11 G), and a 1 : 1 : 1 triplet of 1.34 G. The principal difference between the spectrum of **1a** and that of its deuterated analogue, **1b**, is the replacement of the large doublet of 9.14 G by the 1 : 1 : 1 triplet of 1.34 G. This result reconfirms the assignment[1a)] of $|a(H_5)|=9.14$ G for **1a** and previous estimations of the stable geometry of **1a**;[1a)] **1a** has a pyramidal radical center with C_5–H_5 bent in the exo direction (*i.e.*, $\theta > 0$).

The remaining two sets of doublets of 28.22 and 0.49 G for **1a** should belong to H_{6endo} and H_{6exo}. The C_6–H_{6endo} bond is arranged in a double W-plan[7)] with respect to the odd electron orbital in the stable geometry of **1**, suggesting that $a(H_{6endo})$ is larger than $a(H_{6exo})$. This is consistent with the INDO-UHF calculations.[1a)] Thus the largest doublet of 28.22 G has been assigned to H_{6endo} and the smallest doublet of 0.49 G to H_{6exo}. It should be pointed out that the long-range spin-transfer from the tervalent carbon atom to the two hydrogen atoms on C_6 is highly stereoselective. The remaining three sets of triplets of 0.80, 0.49, and 0.25 G of **1a** are expected to arise from H_1, H_{2syn} and H_{2anti} and their equivalents, but the assignments remain uncertain. Table 1 summarizes the observed hfsc's of **1a** and **1b** together with the assignments.

Temperature Dependence and Isotope Shift of hfsc's. The replacement of H_5 with a deuterium atom shifted not only the splitting pattern attributed to H_5 but also the hfsc's of other protons; a typical example is the increase of the hfsc of H_{6endo} from 28.22 to 28.80 G

Table 1. Observed hfsc's of **1a** and **1b** at −115 °C

Radical	hfsc's (G)[a]					
1a	28.22 d	9.14 d	0.49 d	0.80 t	0.49 t	0.25 t
1b	28.80 d	1.34 t[b]	0.50 d	0.82 t	0.36 t	0.11 t
assignt.	H_{6endo}	H_5	H_{6exo}	(H_1	H_{2anti}	H_{2syn})[c]

a) d: doublet; t: triplet. b) Triplet due to a deuterium nucleus c) The hfsc's of the protons in the parentheses have not been assigned.

upon the deuteration.[1b] The ratio of the observed splitting of [$a(D_5)$ of **1b**]/[$a(H_5)$ of **1a**] at −115 °C is 0.147[1b] which is smaller than that of the magnetic moments of the nuclei (0.1535).

The temperature dependence of the hfsc's of **1a** are illustrated in Figs. 1 and 2. The hfsc's of H_5 and H_{6endo} depend on the temperature (T) as $d|a(H_5)|/dT = 7.9$ mG deg^{-1} and $d|a(H_{6endo})|/dT = -33$ mG deg^{-1}, respectively.

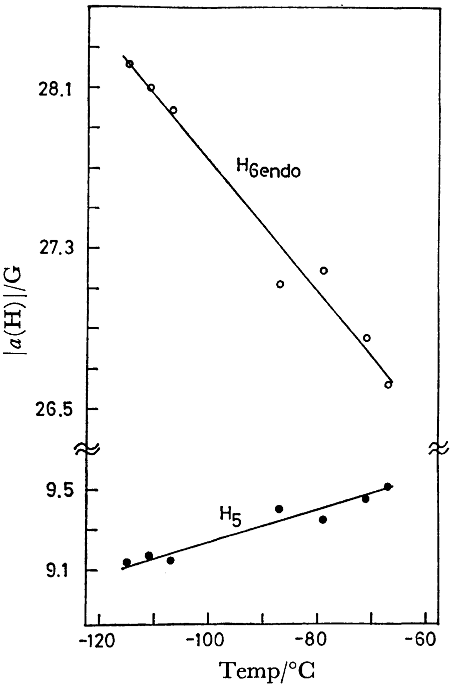


Fig. 1. Temperature dependence of $a(H_5)$ and $a(H_{6endo})$.

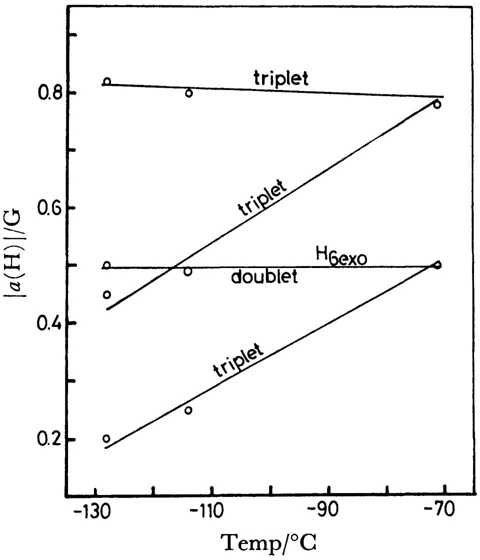


Fig. 2. Temperature dependence of the small hfsc's of **1a**.

The replacement of an α hydrogen atom with a deuterium atom has a similar effect as the lowering of the temperature for the out-of-plane bending mode vibration of the C_α–H_α (or C_α–D_α) bond; both effects decrease the average amplitude of the vibration. Therefore, the small ratio of $a(D_5)$ of **1b** to $a(H_5)$ of **1a** and the positive temperature dependence of $|a(H_5)|$ may be assumed to originate largely from the shift of the average amplitude of the out-of-plane bending vibration of the C_5–H_5 (or C_5–D_5) bond.

The temperature effect on $a(H_{6endo})$ of **1a** may result from the temperature dependence of the out-of-plane bending vibration of the C_5–H_5 bond or of some mode(s) of vibration(s) resulting in a shift of the time-averaged arrangement between the odd electron orbital on C_5 and the C_6–H_{6endo} bond. The observed increase of $a(H_{6endo})$ upon replacement of the H_5 with a deuterium atom was 28.80−28.22=0.58 G, which is similar to the observed increase of the hfsc upon lowering the temperature 15—20 °C. This indicates that the temperature and isotope effects result from the out-of-plane bending mode (and/or the in-plane bending and the stretching modes) vibration of the C_5–H_5 bond. Otherwise, the observed isotope effect on $a(H_{6endo})$ is unreasonably large, since the replacement of H_5 with a deuterium atom has only a small effect on the reduced masses of the other modes of vibrations.

The small triplets of 0.49 and 0.25 G of **1a** (at −115 °C) exhibit a relatively large temperature dependence (Fig. 2). The corresponding splitting of the deuterated analogue, **1b**, at −115 °C are 0.36 and 0.11 G, respectively, which are similar to those of **1a** at a 15 to 20 °C lower temperature. These results indicate that the temperature dependences and deuterium isotope shifts of the hfsc's of **1** may originate largely from the out-of-plane bending vibration of the C_5–H_5 bond.

Procedure for Estimation of the Potential Curve for the Out-of-plane Bending Motion of the C_5–H_5 Bond. The potential curve for the out-of-plane bending vibration of the C_5–H_5 bond may be estimated by reproducing the four experimental values (the temperature dependences and the isotope shifts of the hfsc's of H_5 and H_{6endo}) with trial potential functions.

For this procedure the geometrical dependences of the hfsc's of **1** are required. Calculations using the UHF-INDO method have been shown to give reliable geometrical dependences of the spin distribution. The valence s orbital spin densities on the hydrogen atoms of **1** were calculated at 7.5° intervals of θ, where θ is defined as the angle between the C_5–H_5 bond and the $C_1C_5C_4$ plane. The remaining geometry of **1** is assumed to be the same as the parent hydrocarbon reported by Chiang.[8] The INDO spin densities, ρ, on H_5 and H_{6endo} have been fitted to fourth-order polynomials in θ in order to evaluate ρ at any value of θ desired, and multiplied by C, which converts the spin density into the hfsc:

$$a(\theta) = C(\rho_0+\rho_1\theta+\rho_2\theta^2+\rho_3\theta^3+\rho_4\theta^4). \tag{1}$$

Figure 3 illustrates the calculated geometrical dependence of the hfsc's of H_5 and H_{6endo}. The conversion factor C was set tentatively to 1100 G in Fig. 3.

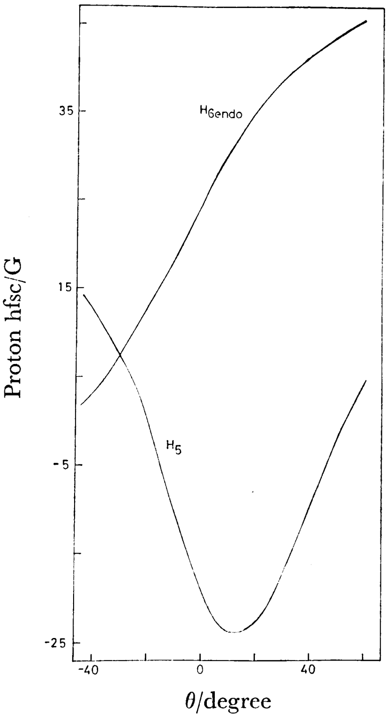


Fig. 3. Geometrical dependence of $a(H_5)$ and $a(H_{6endo})$.

The vibrations of the C_5–H_5 bond have been treated as motions of H_5 bonded to an infinite mass. The hamiltonian for the out-of-plane motion is expressed by the following equation:

$$\mathscr{H} = -\frac{\hbar^2}{2\cdot I}\frac{\partial^2}{\partial\theta^2} + V(\theta) \tag{2}$$

where I is the moment of inertia and $V(\theta)$ an arbitrary potential function which is expressed by an eighth-order polynomial in θ. The eigenfunctions, ϕ_i, are calculated as linear combinations of the lowest twenty eigenfunctions of an appropriate harmonic oscillator that minimizes the difference between the square of the expectation value of the hamiltonian and the expectation value of the square of the hamiltonian in the lowest state,

$$|\langle\phi_0|\mathscr{H}|\phi_0\rangle^2-\langle\phi_0|\mathscr{H}^2|\phi_0\rangle|.$$

The expectation values, $a_i=\langle\phi_i|a(\theta)|\phi_i\rangle$, for each vibrational level i were then calculated using the wave functions obtained for the particular potential. The hfsc of a proton at a given temperature, $a(T)$, is expressed as an average of the expectation values weighted by Boltzmann populations:

$$a(T) = [\sum_i a_i\cdot\exp(-\varepsilon_i/kT)]/[\sum_i \exp(-\varepsilon_i/kT)]. \tag{3}$$

For convenience in the comparison between the experimental and calculated values, the isotope shift of the hfsc of H_5, $\Delta|a(H_5)|$, is defined as shown below from the hfsc's of **1a** and **1b** observed at −115 °C:

$$\Delta|a(H_5)| = [|a(D_5)| \text{ of } \mathbf{1b}]/0.1535-[|a(H_5)| \text{ of } \mathbf{1a}], \tag{4}$$

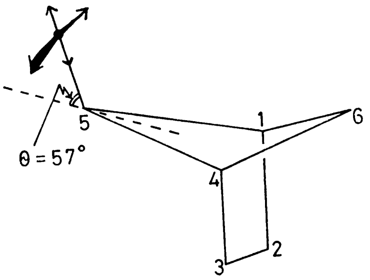
where 0.1535 is the ratio of the magnetic moments of the deuterium nucleus and proton. The isotope shift of the hfsc of H_{6endo} is simply given as the difference between the observed hfsc's of the H_{6endo} of **1a** and **1b** at −115 °C. The temperature coefficient, $d|a(T)|/dT=[|a(T_2)|-|a(T_1)|]/(T_2-T_1)$, and the isotope shift, $\Delta|a(H)|$, are divided by $|a(-115\ ^\circ C)|$ in order to get rid of the somewhat arbitrary multiplication factor, C, in Eq. 1:

$$\begin{aligned} d|A(H)|/dT &= [d|a(T)|/dT]/|a(-115\ ^\circ C)|, \\ \Delta|A(H)| &= \Delta|a(H)|/|a(-115\ ^\circ C)|. \end{aligned} \tag{5}$$

The experimental values are $d|A(H_5)|/dT=+0.86\times10^{-3}\ deg^{-1}$, $\Delta|A(H_5)|=-4.5\times10^{-2}$, $d|A(H_{6endo})|/dT=-1.2\times10^{-3}\ deg^{-1}$, and $\Delta|A(H_{6endo})|=+2.1\times10^{-2}$. From this point $d|A(H)|/dT$ and $\Delta|A(H)|$ are defined as the temperature dependence and isotope shift of the hfsc of a particular proton.

Effect of Vibrations of In-plane Bending and of Stretching Modes of the C_5–H_5 Bond. The wave numbers of the vibrations of the in-plane (or in-cone) bending mode and the stretching mode of the C_5–H_5 bond are expected to be around 1000 and 3000 cm⁻¹, respectively.[9] The energy gaps between these vibrational levels are too large for effective thermal excitation; these vibration modes can not effectively contribute to the temperature dependence of the hfsc's of H_5 and H_{6endo}. However, the replacement of H_5 with a deuterium atom changes the average amplitude of these modes of vibration, possibly resulting in isotope shifts of the hfsc's of H_5 and H_{6endo}.

The isotope shifts of the hfsc's of H_5 and H_{6endo} due to these two modes of vibration have been examined. The motions of the in-plane bending and the stretching vibrations taken into account are shown below:



The angle $\theta=57°$ is the estimated potential minimum for the out-of-plane bending of the C_5–H_5 bond (*vide infra*). The stretching and in-plane bending vibrations have been assumed harmonic with wave numbers in the range 2800—3100 and 800—1500 cm⁻¹, respectively. The geometrical dependence of the spin densities on H_5 and H_{6endo} for these modes of motions may be calculated using the UHF-INDO method and expressed in quadratic forms (*cf*. Eq. 1). The isotope shifts of the hfsc's of H_5 and H_{6endo} due to in-plane bending vibration of C_5–H_5 are then obtained[10] as $\Delta|A(H_5)|=(0.22$—$0.75)\times 10^{-2}$ (-5—-17% of the observed) and $\Delta|A(H_{6endo})|=(0.05$—$0.17)\times 10^{-2}$ (2—8% of the observed). The calculated values of the isotope shifts resulting from the stretching vibration of the C_5–H_5 bond are $\Delta|A(H_5)|=(1.8$—$1.9)\times 10^{-2}$ (-40—-42% of the observed) and $\Delta|A(H_{6endo})|\approx -0.02\times 10^{-2}$ (-1% of the observed). These modes of vibration have negligible effects on the isotope shift of the hfsc of H_{6endo}. These vibrations, however, have quite a large contribution to the isotope shift of the hfsc of H_5, and the estimated contribution of both vibrations are opposite to the experimental observation and also opposite to the contribution of the out-of-plane bending motion (*vide infra*).

The foregoing analyses show that the temperature dependence of the hfsc's of H_5 and H_{6endo} and the deuterium isotope shift of the hfsc of H_{6endo} arise largely from the out-of-plane bending vibration of the C_5–H_5 bond. The isotope shift of the hfsc of H_5 is, however, a result of the counteracting contributions from the out-of-plane bending motion and the stretching and in-plane bending vibrations. Therefore, the isotope shift of the hfsc of H_5 is not such a good indicator as the other three experimental values in the estimation of the potential curve for the out-of-plane bending motion of the C_5–H_5 bond. Calculations, taking only into account the out-of-plane bending vibration, may overestimate the isotope shift of the hfsc of H_5.

Estimation of the Potential Curve. The dependence of the hfsc of H_5 on the pyramidal deformation of C_5 in Fig. 3 reveals that the hfsc of H_5 should be negative, otherwise the radical center must have an unreasonably pyramidal geometry. Thus the hfsc of H_5 has been assumed negative. Based on this assumption the observed positive temperature dependence of the absolute value of the hfsc of H_5 indicates that the potential curve for the out-of-plane vibration of C_5–H_5 bond is anharmonic.[5a,5e] Several typical trial anharmonic potential functions, selected from more than thirty trials, are illustrated in Fig. 4. Table 2 summarizes the calculated temperature dependences and isotope shifts of the hfsc's of H_5 and H_{6endo}.

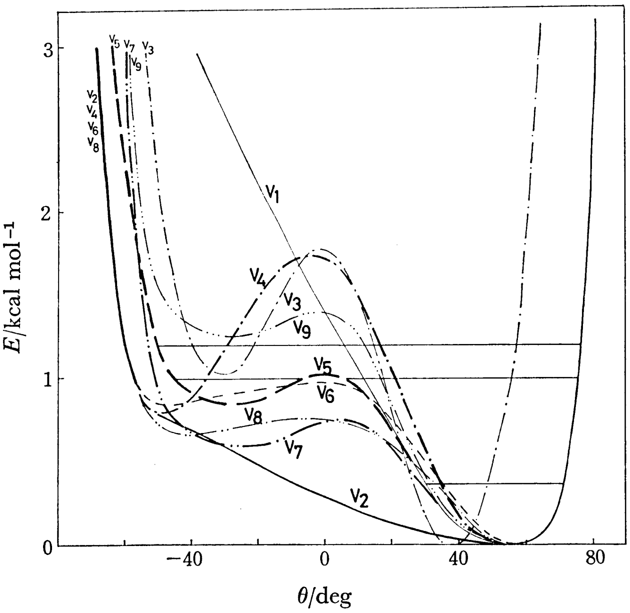


Fig. 4. Trial potential curves. Horizontal solid lines are vibrational levels calculated with curve V_5 for **1a**.

Simple single-minimum anharmonic potential curves (V_1, V_2) gave calculated values which were too small for the temperature dependence of the hfsc of H_{6endo}. The reason for this is that the expectation values of $a(H_{6endo})$ for the second and higher vibrational levels of **1a** are not sufficiently shifted from the lowest vibrational level to reproduce the observed large temperature dependence of $a(H_{6endo})$. In order to reproduce the experimentally observed large negative temperature dependence of the hfsc of H_{6endo}, the lowest vibrational level needs to be restricted in the positive range of θ, whereas in the second and higher excited vibrational levels, the extent of the vibration of C_5–H_5 bond needs to be extended to a very large negative value of θ. Such requirements can be satisfied by unsymmetrical double-minimum potential curves. ΔE (kcal/mol) is defined as the difference between the two minima and $\Delta\varepsilon$ (kcal/mol) as the barrier to inversion measured from the higher minimum. Double-minimum potential curves with relatively high barrier to inversion (V_3, V_4)

Table 2. CALCULATED TEMPERATURE DEPENDENCES AND ISOTOPE SHIFTS OF hfsc's OF H_5 AND H_{6endo}

Curve	$d\|A(H_{6endo})\|/dT$[a]	$d\|A(H_5)\|/dT$[a]	$\Delta A(H_{6endo})$[a]	$\Delta A(H_5)$[a]	ΔE[b]	$\Delta\varepsilon$[b]
V_1	15	229	40	341	c)	c)
V_2	68	−154	76	94	c)	c)
V_3	62	−127	54	22	0.95	0.75
V_4	26	235	46	458	0.79	0.96
V_5	76	76	142	246	0.89	0.18
V_6	104	88	92	494	0.87	0.15
V_7	92	−1.5	361	−43	0.60	0.20
V_8	104	d)	92	413	0.66	0.10
V_9	29	208	48	341	1.30	0.17
obsd	-1.2×10^{-3}	0.86×10^{-3}	2.1×10^{-2}	-4.5×10^{-2}	—	—

a) Calculated values are given as a per cent of the experimental values. b) In kcal/mol.
c) Single-minimum. d) Not monotonous and very small.

predict a too small temperature dependence and a too small isotope shift of the hfsc of H_{6endo}.

The potential curves with a ΔE of around 0.9 kcal/mol and a relatively low barrier to inversion (V_5, V_6) give reasonable temperature dependences of the hfsc's of H_5 and H_{6endo} and an acceptable isotope shift for H_{6endo}. The isotope shifts of the hfsc of H_5 calculated with V_5 and V_6 are acceptable since the contributions of the in-plane and stretching vibrations to the isotope effects on $a(H_5)$ (*vide supra*) have been ignored. Potential curves with small values of ΔE gave an unacceptable small temperature dependence of $a(H_5)$ (V_7, V_8) and a curve with a large value of ΔE gave a too large temperature dependence of $a(H_5)$ (V_9).

Thus the potential curve for the out-of-plane vibration of C_5–H_5 bond is suggested as a double-minimum potential with a small barrier to inversion with an energy difference of around 0.9 kcal/mol between the two energy minima. The geometry with the C_5–H_5 bond tilting in the exo direction is about 0.9 kcal/mol more stable than that with the C_5–H_5 bond located on the endo side. The barrier to inversion, $\Delta\varepsilon$, is very small and there is no vibrational steady state in which the C_5–H_5 bond is localized in the endo side of the $C_1C_5C_4$ plane ($\theta<0$); even the zero-point vibrational level in the left well ($\theta<0$) is located above the barrier top and effectively mixed with the vibrational state(s) in the right well ($\theta>0$).

Estimation of the Potential Curve. The dependence of $a(H_{6endo})$ on the out-of-plane deformation angle, θ, is large and monotonic. This feature was helpful in estimating the potential curve of the out-of-plane vibration of C_5–H_5 bond. However, in the case of most alkyl radicals, the parameters available for estimation of the potential curve would be only the temperature dependence of the hfsc of α proton(s). In such cases, it would be impossible to estimate the potential curve only from the temperature dependence of the hfsc of the α proton(s). For example in the case of the present radical, the results in Table 2 show that at least three potential curves would give acceptable temperature dependence of the hfsc of H_5: a single-minimum curve lying between V_1 and V_2, a double-minimum curve with a relatively high barrier to inversion lying between V_3 and V_4, and a double-minimum potential with a low barrier to inversion similar to V_5 or V_6.

Experimental

ESR Measurements. The ESR spectra of **1a** and **1b** were obtained during photolysis of bis(bicyclo[2.1.1]hexane-5-carbonyl) peroxide and bis(5-deuteriobicyclo[2.1.1]hexane-5-carbonyl) peroxide, respectively. The solvent was deoxygenated liquid cyclopropane. Measurements were conducted on a JEOL PE-2X spectrometer modified with a JEOL ES-SCXA gunn diode X-band microwave unit equipped with a cylindrical mode cavity with slits for UV irradiation. The field sweep was monitored during each ESR measurement with ^1H NMR using a water sample, which was set just outside the ESR cavity. A tunable NMR radio frequency was supplied from a JEOL ES-FC3 oscillator and counted on a Takeda-Riken TR-5501 frequency counter. The magnetic field difference between the ESR and NMR sample position was calibrated daily with perylene cation in concentrated sulfuric acid. ($g=2.002583$).[11] Photolysis was performed with a Philips SP-500 super-high-pressure mercury lamp focused with two quartz lenses and filtered through a distilled water cell of 45 mm path length. Accumulations and simulations were performed using a JEOL JEC-6 minicomputer.

The g factor and hfsc's were corrected against the microwave frequency drift,[12] which may result from the heating of the cavity by radiation and/or the change of chemical constituents in the sample through photochemical reactions.

The ESR samples were cooled with a cold nitrogen gas flow controlled by a JEOL JES-VT-3A temperature controller. The heating of samples by radiation was calibrated by measuring the temperature of liquid cyclopropane in a sample tube during irradiation and the temperature of the cooling nitrogen gas.

For the measurements of the isotope shifts of the hfsc's, the spectrum of **1b** was measured immediately after observation of the spectrum of **1a** without any change in the setting of the temperature of the nitrogen gas flow cooling the sample.

Bicyclo[2.1.1]hexane-5-carbonyl Chloride. A mixture of bicyclo[2.1.1]hexane-5-carboxylic acid[13] (3.0 g, 24 mmol) and thionyl chloride (8.7 g, 73 mmol) in chloroform (14 ml) was refluxed for 4 h. The chloroform was removed by distillation under atmospheric pressure. Distillation of the residue gave a forerun of the excess thionyl chloride (52—54 °C/400 Torr) followed by bicyclo[2.1.1]hexane-5-carbonyl chloride (2.8 g 19 mmol) (bp 68—74 °C/21 Torr); yield 80 %.

Bis(bicyclo[2.1.1]hexane-5-carbonyl) Peroxide. To a suspension of sodium peroxide (290 mg, 3.7 mmol) in dry ether (12 ml) cooled in an ice bath was added a solution of bicyclo-[2.1.1]hexane-5-carbonyl chloride (1.0 g, 6.9 mmol) in dry ether (8 ml) and two drops of water. The mixture was stirred overnight in an ice bath and then at room temperature for several hours followed by the dropwise addition of cold water (20 ml) to dissolve the excess sodium peroxide and the generated sodium chloride. The ethereal layer was washed with a saturated sodium hydrogencarbonate aqueous solution and then with a sodium chloride aqueous solution and finally dried over anhydrous magnesium sulfate. The ether was evaporated to dryness by a flow of nitrogen gas; yield 50 %. The white crystalline peroxide was stored as a pentane solution (or suspension).

5-Deuteriobicyclo[2.1.1]hexane-5-carboxylic Acid. A solution of norbornane diazo ketone[13] (3.5 g, 0.026 mol) in a mixed solvent of 1,4-dioxane (70 ml) and D_2O (50 ml) was irradiated under nitrogen with a 200 W medium-pressure mercury lamp. The course of the reaction was monitored by the disappearance of the diazo band at 4.80 μm in the infrared absorption, and required about 1.5 h. Approximately 100 ml of the mixed solvent was removed by distillation through a 30-cm Vigreux column under reduced pressure (bp 43—44 °C/100 Torr). The residue was made alkaline with 1 M sodium hydroxide and extracted with three 50 ml portions of ether to remove the neutral materials. The aqueous solution was acidified with hydrochloric acid and extracted with four 50 ml portions of ether, and dried over anhydrous magnesium sulfate. The ether solvent was removed and distillation of the residue gave 0.88 g of 5-deuteriobicyclo[2.1.1]hexane-5-carboxylic acid, bp 106—109 °C at 7 Torr; yield 27 %.

Bis(5-deuteriobicyclo[2.1.1]hexane-5-carbonyl) Peroxide. The 5-deuteriobicyclo[2.1.1]hexane-5-carboxylic acid was converted to the acid chloride with thionyl chloride and treated with sodium peroxide to obtain the peroxide.

The authors would like to thank Dr. S. Kato (Institute of Molecular Science) for the computer program to solve the anharmonic oscillation. This work was partly supported by a grant from the Ministry of Education. INDO-UHF calculations are performed with FACOM M190 computer at Data Processing Center of Kyoto University.

Note Added in Proof

The potential curve for the out-of-plane bending motion of the C_5–H_5 bond of **1** was calculated with *ab initio* UHF method. Basis functions were the STO-3G set[14] except those for the tervalent carbon atom, for which Dunning's 4s/2p basis set[15] was adopted. The calculated curve resembles the curve V_3 in Fig. 4. The extrema of the calculated curve are (θ deg, E kcal/mol): (-22, 1.2), (7, 2.1), and (42, 0.0). This result is consistent with the present conclusion.

We thank Dr. H. Nakatsuji and Mr. K. Ohta (Kyoto) for discussions and Gauss-70 program. *Ab initio* calculations were performed on HITAC M-180 computer at Institute of Molecular Science.

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