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A LONG-RANGE ISOTOPE EFFECT ON A HFSC OF THE BICYCLO[2.1.1]HEXAN-5-YL RADICAL

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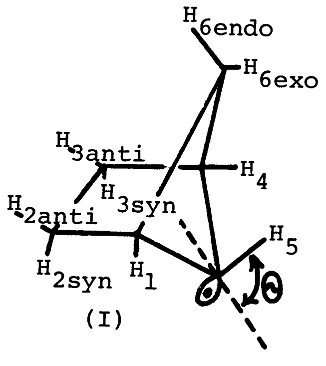
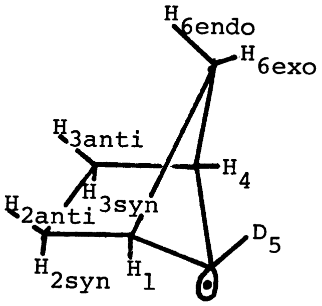
The hyperfine splitting constant (hfsc) of H_{6endo} of the bicyclo[2.1.1]hexan-5-yl radical increased from 28.22 G to 28.80 G upon the replacement of H_5 with a deuterium atom, which is qualitatively explained, with the aid of INDO calculations, as due to the decrease of the out-of-plane mode vibration of the C_5-H_5 bond upon the replacement.

Potential curves for out-of-plane mode vibrations around radical-center carbon atoms of alkyl radicals have been extensively studied by examining temperature and isotope effects on hyperfine splitting constants (hfsc) of α-carbon atoms and α-protons.[1] In this communication we report a long-range isotope effect and temperature-dependence of the H_{6endo} hfsc of the bicyclo[2.1.1]hexan-5-yl radical[2] (I) and their qualitative analysis on the basis of a potential curve and geometrical dependences of proton hfsc's calculated with INDO method.[3]



(I)



(II)

The spectrum of I (Figure 1A) was observed during photolysis of a cyclopropane solution of bis(bicyclo[2.1.1]hexane-5-carbonyl) peroxide at -115°. The largest two hfsc's of I and their assignments are $|a(H_{6endo})| = 28.22$ G and $|a(H_5)| = 9.14$ G.

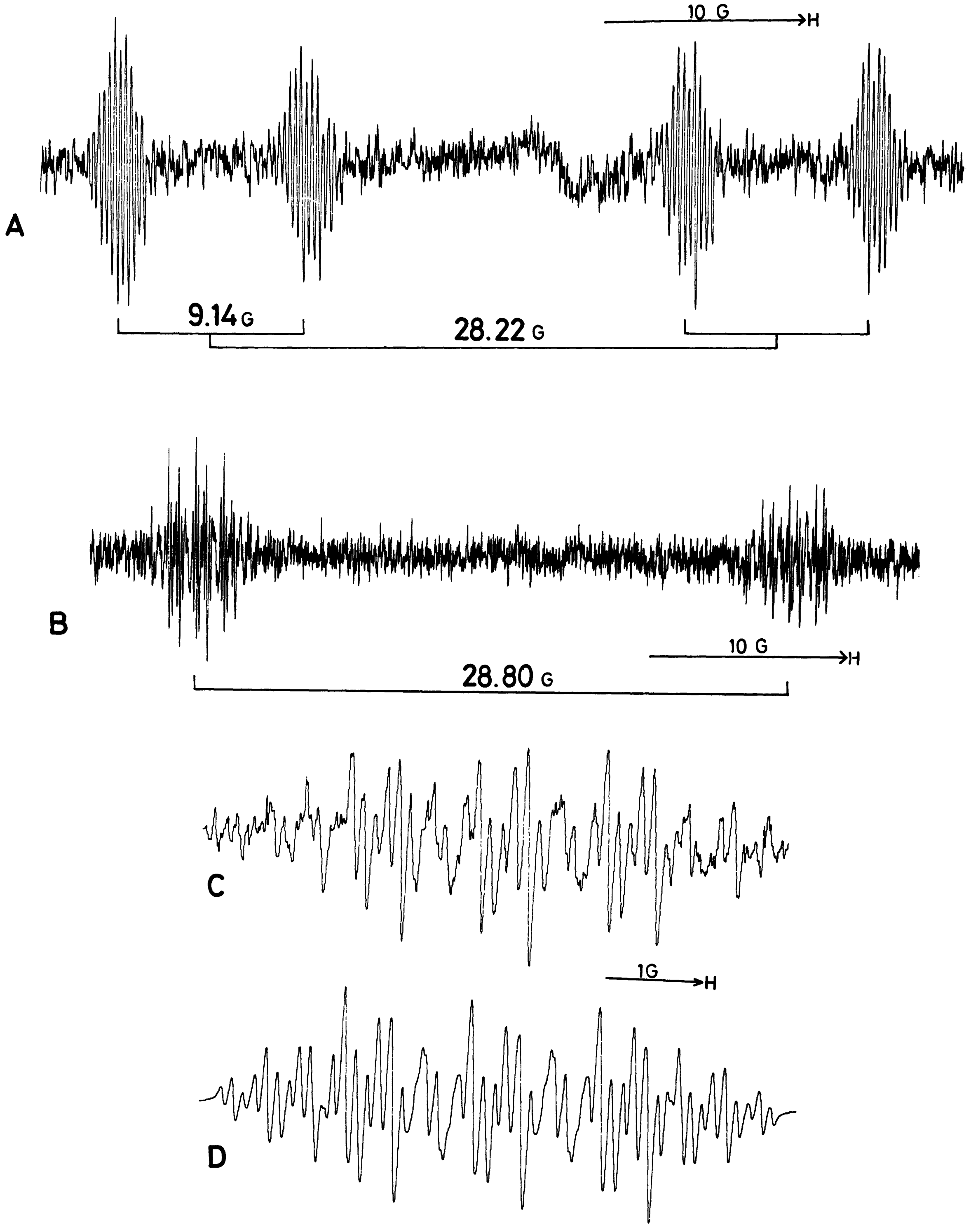


Fig. 1. A) ESR spectrum of I at -115° ; B) ESR spectrum of II at -115° ; C) the low field groups of B obtained by four accumulations ; D) the simulated spectrum corresponding to C.

Figure 1B shows the spectrum of 5-deuteriobicyclo[2.1.1]hexan-5-yl radical (II) photochemically generated from bis(5-deuteriobicyclo[2.1.1]hexane-5-carbonyl) peroxide at -115°. The lower field group of absorptions of Figure 1B was examined with computer averaging technique (Figure 1C). The absorptions due to II are analyzed as two sets of doublets (28.80 and 0.50 G) split into three sets of 1:2:1 triplets (0.82, 0.36, and 0.11 G) further into 1:1:1 triplets of 1.34 G. The simulated spectrum (Figure 1D) coincides well with the observed spectrum. Assignments of $|a(H_{6endo})|=28.80$ G and $|a(D_5)|=1.34$ G are straightforward. The ratio of the observed splittings of [$a(D_5)$ of II]/[$a(H_5)$ of I] was 0.147 for II. This is smaller than that of the magnetic moments of the nuclei (0.153). The hfsc of H_{6endo} increased 0.58 G upon the replacement of H_5 with a deuterium atom. To our knowledge, this is the first example of a long-range isotope effect on a hfsc.

Figure 2 illustrates the observed temperature-dependences of the H_5 and H_{6endo} hfsc's of I. The absolute values of the H_5 and H_{6endo} hfsc's have a positive and a negative temperature-dependence, respectively. The temperature-dependence of the H_5 hfsc is well expected as originating from the temperature-dependence of the average amplitude of the out-of-plane mode vibration of the C_5-H_5 bond. This is supported with the observed isotope effect on $a(H_5)$, i.e. the ratio of [$a(D_5)$ of II]/[$a(H_5)$ of I] is smaller than the ratio of nuclear magnetic moments of the nuclei and this is in parallel with the positive temperature-dependence of $|a(H_5)|$.

Possible sources of the temperature effect on $a(H_{6endo})$ is the temperature-dependent change of the average vibrational amplitude either of the angle between the C_5-H_5 bond and the $C_1C_5C_4$ plane or some modes of vibration resulting in a change in the C_5-C_6 distance. However, only the former mechanism is consistent with the observed increase of $a(H_{6endo})$ upon the replacement of H_5 with a deuterium atom.

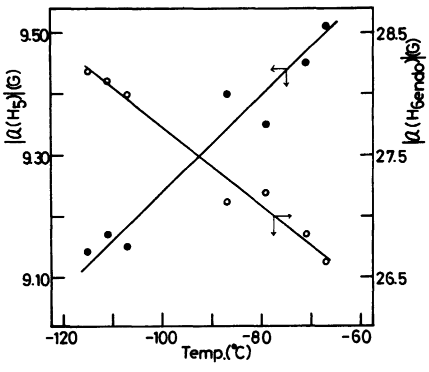


Fig. 2. The temperature dependence of $|a(H_5)|$ (●) and $|a(H_{6endo})|$ (○).

Figure 3 shows the total energy, $a(H_5)$ and $a(H_{6endo})$ of I calculated as functions of θ with the INDO method,[3] where θ is the angle between the C_5-H_5 bond and the $C_1C_5C_4$ plane. The calculated anharmonic potential curve indicates that the average value of θ increases with the decreasing thermal excitation (i.e. lowering of temperature) of the out-of-plane vibration of the C_5-H_5 bond. The vibrational energy levels of the deuterated radical (II) are always lower than the corresponding levels of the radical (I) because of the difference in the moments of inertia. The replacement of H_5 in radical (I) with a deuterium atom has, therefore, the same effect on the out-of-plane vibration as the decrease of the temperature. Thus the present analysis based on INDO results in Figure 3 indicates that both the decrease of the temperature and the substitution of H_5 with a deuterium atom induces the increase of θ resulting in the increase of $|a(H_{6endo})|$ and the decrease of $|a(H_5)|$, and this is qualitatively consistent with the experimental results.

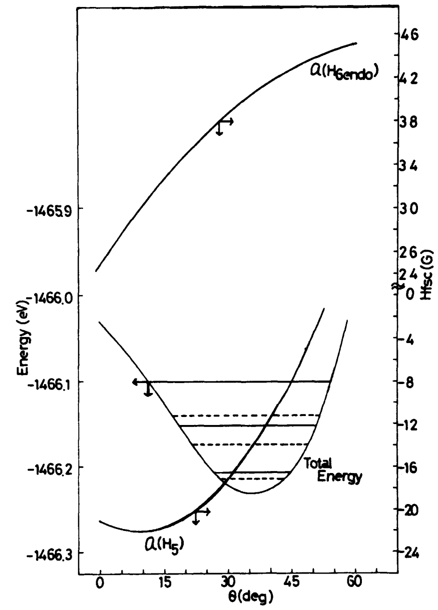


Fig. 3. Calculated total energy, $a(H_5)$ and $a(H_{6endo})$ of I as function of θ. Straight lines are the vibrational energy levels of I and dashed lines are the corresponding levels of II.

We conclude that the out-of-plane vibration of the C_5-H_5 bond induces the temperature dependence as well as the long-range isotope effect on $a(H_{6endo})$ through a sharp dependence of $a(H_{6endo})$ on the angle between the C_6-H_{6endo} bond and the axis of the odd electron orbital on C_5. We would like to also point out that the anharmonicity of the potential for the out-of-plane vibration of the C_5-H_5 bond is essential to explain the temperature-dependence and the isotope effect of $a(H_5)$.

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