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MAGNETIC ANISOTROPY OF THE CYCLOBUTANE SYSTEM WITH A PUCKERED STRUCTURE

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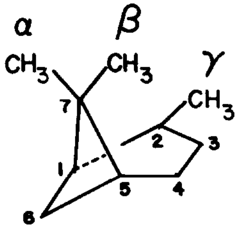
The present paper deals with a report on the magnetic anisotropy of a cyclobutane ring having a puckered structure. The chemical shifts of three methyl groups in pinane (I) and its derivatives measured by using a Varian A-60 spectrometer (10% carbon tetrachloride solution, internal ref. TMS.) are summarized in Table 1. As shown in the Table, the shielding constants of α-methyl groups in pinane and its derivatives are not affected by the substituents at positions 2,3 and 4, whereas the chemical shifts of β- and γ-methyl groups are changed by them. In the compounds with cis-configuration between their methyl groups at positions 2 and the gem-dimethyl groups, the signals of β- and γ-methyl groups are shifted to a lower magnetic field than those of the trans-isomer, as a result of van der Waals' force[1-4, 16-18)] owing to the proximity of their methyl groups. For example, each of the β- and γ-methyl resonances of cis-pinane suffers an appreciable lower field shift (0.14 ~ 0.18 ppm.) than those of the trans-isomers. The downfield shift due to van der Waals' force is expressed in equation 1*



I

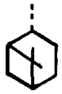
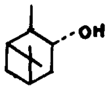
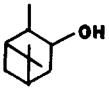
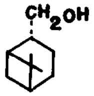
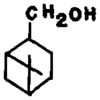
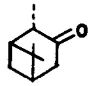
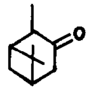
$$\sigma_W = -\frac{[R]}{r^6} \times 7 \text{ ppm} \qquad (1)$$

From equation 1, it is suggested that β- and γ-methyl resonances of cis-compounds are shifted downfield by about 0.2 ppm.

α-Methyl proton resonance signals in all the pinane derivatives appear at approximately 0.4 ppm lower fields than those of β-methyl groups as shown in Table 1, if we exclude the influences of the functional groups.

TABLE I

Chemical Shifts of Methyl Groups in Pinanes

Compounds	Methyl Protons in τ			Compounds	Methyl Protons in τ		
	γ	α	β		γ	α	β
	9.13*	8.80	9.16		8.91*	8.80	9.09
	8.99*	8.80	8.98		8.93*	8.82	8.94
	8.35	8.73	9.16		6.73**	8.78	9.14
		8.77	9.28		6.58**	8.83	9.05
	8.97*	8.64	9.09		8.73	8.73	9.06
	8.85*	8.67	9.13				

* Doublet

** Methylene protons of the hydroxy methyl group

Equation 1 is derived in the following manner. The van der Waals' potential, U_1, between particles A and B is shown in equation 1′ where α_A and α_B are their polarizabilities, $h\nu$ is the mean excitation energy ($\nu = 2\, \nu_A\, \nu_B / (\nu_A + \nu_B)$) and r is the distance between them.

$$U_1 = - 3\, \alpha_A\, \alpha_B\, h\nu / 4\, r^6 \qquad (1')$$

On the other hand, the particle A which is in an electric field E has the potential energy U_2. A new equation 3′5) is obtained from the two equations 1′ and 2′, if it is possible to assume $U_1 = U_2$.

$$U_2 = - \alpha_A\, E^2 / 2 \qquad (2') \qquad E^2 = 3\, \alpha_B\, h\nu / 2\, r^6 \qquad (3')$$

According to Marshal's calculation6), the low field shift due to an electric field or σ_E is expressed as follows:

$$\sigma_E = - 881\, a_0^3\, E^2 / 216\, mc^2 \qquad (4')$$

where a_0, m, and c are Bohr's radius, mass of electron and light velocity, respectively. Using the relationship where $h\nu = 10$ e.v., r in Å-unit and $\alpha_B = 3\, [R] / 4\pi N$ in which [R] is the atomic refraction of B atom and N is Avogadro's number, the low field shift caused by van der Waals' force for hydrogen atom A or σ_W is expressed as shown in equation 1.

Similarly, the protons of methylene and methine groups at positions 2,3 and 4 in the compounds resonate at the τ 7.5 $\sim$ 8.5. This resonance field is lower by about 0.5 ppm in comparison with those of the bornane and carane derivatives. In some cyclobutane derivatives having bulky functional groups or rigid structures, such as $C_4 Cl_8$ 7), anemonin 8), pinanes 9) and 1,2-dibromo-1,2-dicarbomethoxycyclobutanes 10), the four-membered ring was reported to be puckered. Therefore, quasi-axial and equatorial directions in such a cyclobutane ring should be considered. From the experimental results shown in Table 1, there seems to be a paramagnetic anisotropy in the axial direction at the carbon atoms of the cyclobutane ring.

In addition to the pinane derivatives, there are other examples that indicate downfield shifts of axial protons in such a system. For example, axial protons at carbon atoms of the cyclobutane ring in bicyclo[2.1.1]hexanes 11) resonate at fields lower by 1.0 ppm than equatorial protons, and methylene hydrogens (τ = 8.18) in an axial direction of the compound shift downfield by 0.31 ppm, as compared with cyclopentane (τ = 8.49).

These experimental observations appear to suggest that the low-field shift area is located in the axial direction of the cyclobutane ring having a puckered structure as shown in Fig. 1, whereas a relatively high field shift area is in the equatorial bearings.

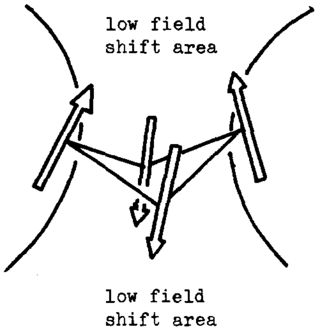


FIG. I

Magnetic anisotropy in the cyclobutane ring
with a puckered structure

The magnetic nature in cyclobutane ring system may be explained in terms of anisotropy due to the atomic paramagnetic current as in the case of C=C and C-C carbons 12). According to the calculation of atomic susceptibility by means of Pople's method 13) with a mean excitation energy, it is concluded that C-C carbon atoms do not have any atomic anisotropies. However an anisotropic effect may be expected even in C-C carbons, if various excitation energies are adopted. For example, when the energy relationship of cyclohexane systems is as presented in equation 2, the susceptibility of a singly bonded carbon atom is described in the order of $\chi^{c}_{xx} > \chi^{c}_{yy} > \chi^{c}_{zz}$, i.e. axial ring protons in the Z-direction in Fig. 2 absorbed at a higher magnetic field** than their epimeric equatorial counterparts in the X-direction.

On the other hand, since the C-C bond energy of cyclobutane rings[15)] is smaller than that of cyclohexane systems, the excitation energies seem to have a relationship as expressed in equation 3. In this case, the atomic susceptibility may be arranged in the order of $\chi_{xx} < \chi_{yy} < \chi_{zz}$.

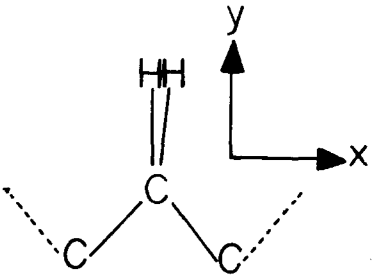


Fig. 2

$$\left|\Delta E_{CH-CH*}\right| < \left|\Delta E_{CH-CC*}\right| \cong \left|\Delta E_{CC-CH*}\right| < \left|\Delta E_{CC-CC*}\right| \qquad (2)$$

$$\left|\Delta E_{CH-CH*}\right| > \left|\Delta E_{CH-CC*}\right| \cong \left|\Delta E_{CC-CH*}\right| > \left|\Delta E_{CC-CC*}\right| \qquad (3)$$

If the above-mentioned assumption is acceptable, it may be possibly concluded that the axial protons in the Z-direction are subjected to a shift to lower fields than the equatorial protons in the X-direction. The cyclobutane rings, therefore, having puckered structures should have the effective field as depicted in Fig. 1.

** The second-order hyperconjugation[14)] of vicinal protons of $C\!<^{H}_{H}$ group may also contribute to the difference of the shielding constant between the axial and equatorial protons in the systems.

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