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# EFFECTS OF PARAMAGNETIC SHIFT REAGENTS ON THE ROTATION OF AN ISOPROPYL GROUP

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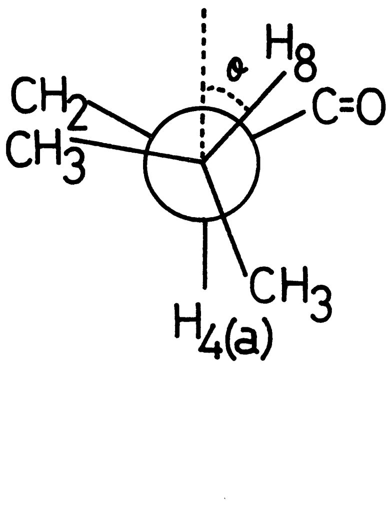
Observed effects of shift reagents on the rotation of an isopropyl group are reported for two substrate molecules, menthol and menthone, using Eu(DPM)$_3$. The free energies of activation $\Delta G^{\ddagger}$, obtained from the rotation of the isopropyl groups in menthol- and menthone-Eu(DPM)$_3$ complexes are described.

The application of lanthanide shift reagents to NMR spectroscopy, first introduced by Hinckley$^{1)}$ in 1969, has been an effective and general technique for resolving structural problems of organic compounds. In this paper, observed effects of shift reagents on the rotation of an isopropyl group are reported for two substrate molecules, menthol and menthone, using the most popular shift reagent, tris(dipivalomethanato)europium (hereafter abbreviated to Eu(DPM)$_3$).

The continuous variation method described by Roth et al.$^{2)}$ was applied to determine the stoichiometry of Eu(DPM)$_3$ complex. In the case of menthol, $\Delta\delta\cdot C_s$, the scale of the concentration of the complex in equilibrium, takes a maximum value at $C_{Eu}/(C_s + C_{Eu}) = 0.50$, which indicates the formation of a 1:1 complex.

The coefficients of correlation between the molar ratios m ($=C_{Eu}/C_s$) and the induced chemical shifts of various protons in menthol and menthone were about 1.00 ± 0.01. It was reported$^{2)}$ that the induced chemical shift $\Delta\delta$ converged or reached a maximum with an increase of m-value, whereas the results described above demonstrates the linearity in accord with earlier findings$^{1)}$ in the region of $m < 1.0$.



The location of the $Eu^{3+}$ ion was studied on the theory that induced shifts are dominated by the pseudocontact interaction. The relation between the induced shift $\Delta\delta$ and the average distance from the $Eu^{3+}$ ion, R, to the considered proton in the metal chelate-organic substrate complex is indicated in Eq. 1,[3] where K is a constant for any given molecule at a known temperature and $\phi$ (the angle between the

$$\Delta\delta = K\,(3\cos^2\phi_i - 1\,)\,/\,R_i^3 \qquad \text{(Eq. 1)}$$

$i$ th proton and principal axis) is assumed negligible if we follow Hinckley's approximation.[1] The geometry of menthol and menthone was determined with the help of several references.[4] The correctness of the coordinate was confirmed with the total energies calculated by the Extended Hückel Molecular Orbital method.[5] Eq. 1 was applied to some protons of menthol and menthone ($2\text{-}H_a$, $2\text{-}H_e$ and $7\text{-}CH_3$ protons of menthol; $2\text{-}H_a$, $4\text{-}H_a$ and $7\text{-}CH_3$ protons of menthone), and the position of $Eu^{3+}$ ion was calculated to be 3.0 and 3.0 Å from the alcohol oxygen and the carbonyl oxygen, respectively. When these results were applied to methyl protons of isopropyl group ($9\text{-}CH_3$ and $10\text{-}CH_3$ protons both in menthol and menthone), good accord was not obtained when their conformations were most stable, $\theta = 0°$ , calculated by the EHMO method. These facts were due to the hindered rotation of isopropyl groups in menthol and menthone, and the rotational angles in both substrates were shown to be 58° from

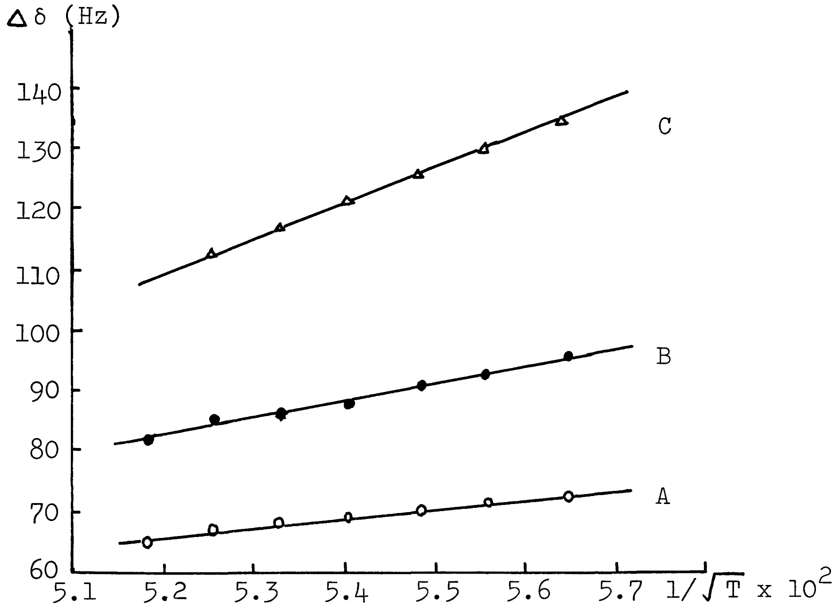
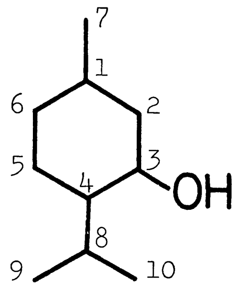


Fig. 1 Relation between $\Delta\delta$ and temperature (°K) in $7\text{-}CH_3$ of menthol: A; m (molar ratio of $Eu(DPM)_3$ /menthol) =0.19, B; m=0.35, C; m=0.77.



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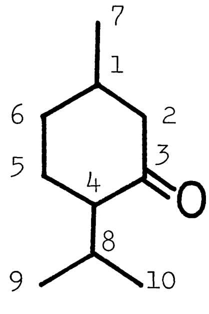

menthone

Table 1. $\Delta G^{\ddagger}$ for the rotation of an isopropyl group.

| substrate | solvent | m** | $T_c$(°K) | $\Delta G^{\ddagger}$(kcal/mole) |
|---|---|---|---|---|
| menthol | $CCl_2=CCl_2$ | 0.19 | 389 | 21 |
| menthol | $CCl_2=CCl_2$ | 0.35 | 469* | 24 |
| menthol | $CCl_2=CCl_2$ | 0.77 | 479* | 24 |
| menthone | $C_6H_5Br-d_5$ | 0.21 | 319 | 18 |
| menthone | $C_6H_5Br-d_5$ | 0.44 | 357 | 20 |
| menthone | $CCl_2=CCl_2$ | 0.44 | 418* | 22 |

*; extrapolated value,

**; molar ratio of $Eu(DPM)_3$/substrate,

the most stable conformations.

Temperature-dependent NMR spectra were measured in order to survey the rotation of isopropyl groups in more detail. When the induced shifts of 7-$CH_3$ protons of menthol in various molar ratios of $Eu(DPM)_3$/substrate are plotted against $1/\sqrt{T}$ , straight lines are obtained as shown in Fig. 1, which is in accordance with the result reported by Beaute *et al*.6) This means that a collision-type complex takes an important factor, in spite of the aid of the pseudocontact shift equation in structural studies.

The chemical shifts of the two resonances in isopropyl groups, 9-$CH_3$ and 10-$CH_3$, are examined by varying the temperature. The chemical shift between the two methyl resonances began to decrease at a temperature of 343°K, and was reduced to zero at 389°K in the case of menthol in tetrachloroethylene. In the case of temperature higher than the coalescence temperature $T_c$ the free rotation about the C-C bond of the isopropyl group will proceed. The rate constant $k_c$ at the coalescence temperature can be easily obtained7); and the consideration of the absolute rate equation enable us to calculate the free energies of activation $\Delta G^{\ddagger}$. As is shown in Table 1, every $\Delta G^{\ddagger}$, obtained from the rotation of isopropyl groups in menthol- and menthone-$Eu(DPM)_3$ complexes are about 20 kcal/mole with the studied solvents and concentrations.8) These large values seem to include the enthalpies (about 10 kcal/mole) at the equilibrium of the formation of the collosion-type complexes, which was calculated from Fig. 1.

## References

1) C. C. Hinckley, J. Amer. Chem. Soc., **91**, 5160 (1969) .

2) K. Roth, M. Grosse, and D. Rewicki, Tetrahedron Lett., 435 (1972).

3) H. M. McConnell and R. E. Robertson, J. Chem. Phys., **29**, 1361 (1958).

4) N. L. Allinger, M. T. Tribble, and M. A. Miller, Tetrahedron, **28**, 1173 (1972); Tables of Interatomic Distances and Configuration in Molecules and Ions, the Chemical Society (London), special publication Nos. 11 (1958) and 18 (1965).

5) K. Yamada, S. Ishihara, and H. Iida, J. Faculty of Engineering, Chiba Univ., **24**, 55 (1972).

6) C. Beaute, S. Cornuel, D. Lelandais, N. Thoai, and Z. W. Wolkowski, Tetrahedron Lett., 1099 (1972).

7) H. Kessler, Angew. Chem. internat. Edit., **9**, 219 (1970).

8) The 5th Symposium of Structural Organic Chemistry, Nagoya, 1972, No. 1-10.

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