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STUDIES OF STERIC EFFECTS. SPECTROSCOPIC EVIDENCE FOR THROUGH-SPACE INTERACTION IN CH_3 ---- O IN CROWDED ALCOHOLS

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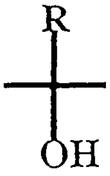
Abstract: Through-space interaction of the γ-methyl hydrogen with the oxygen atom in crowded tertiary aliphatic alcohols generates an abnormally low-field chemical shift in the ^{17}O NMR spectra. The intramolecular through-space attractive interaction or hydrogen bonding interaction between the γ-methyl hydrogen and the oxygen lone pair (CH_3 ---- O) is proposed as the cause of this shift. By this interaction, the less polar C-O bond is generated.

In sterically crowded molecules, interesting phenomena are caused by the steric effects in chemical reactions[1)] and NMR chemical shifts.[2)]

Tezuka et al. recently proposed a steric reverse polarization-reaction (STECAR) effect,[3)] namely that the through-space attractive gauche-orbital interaction of the heteroatom lone pair of the C-X bond with the γ-methyl hydrogen at a fixed conformation in crowded carbinyl compounds generates a specific electron distribution at the interacting hetero atom or a less polar C-X bond, thereby causing specific ionic reactions. This prompted us to study electronic properties of crowded compounds NMR spectroscopically.[4)]

In this study, the measurements of ^{17}O and ^{13}C NMR spectra of several crowded alcohols revealed a very interesting finding with regard to the steric effect on NMR chemical shifts. This paper presents evidence for the attractive CH_3 --- O interaction and generation of the less polar C-O bond in crowded alcohols.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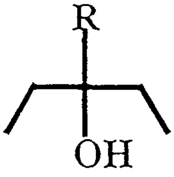
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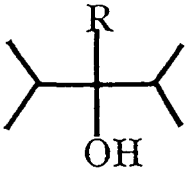
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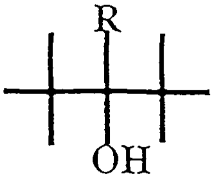
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R = a: CH_3; b: CH_2CH_3; c: $CH(CH_3)_2$; d: $C(CH_3)_3$

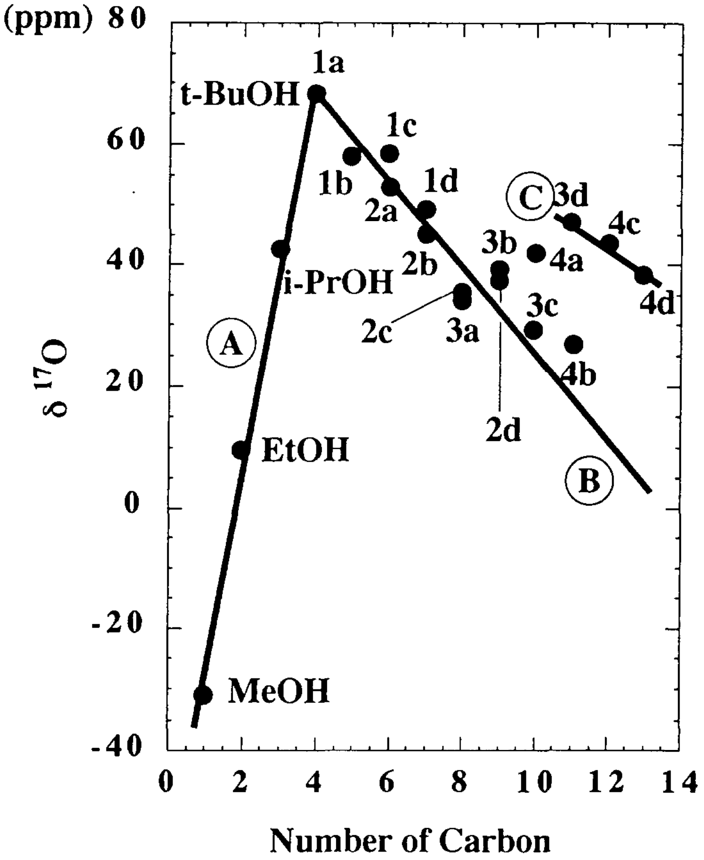
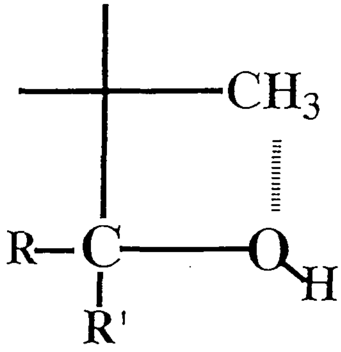


Fig 1. The correlation of ^{17}O chemical shifts of alcohols with the number of carbon atoms (δ : ppm from external D_2O)

Several tertiary aliphatic alcohols *(1- 4)* were prepared by the usual methods using alkyl metals and ketones with some modification in the case of highly crowded compounds. These compounds were confirmed spectroscopically and by elemental analyses of their *para*-nitrobenzoates. ^{17}O NMR spectra of these alcohols were measured in chloroform-d at 67.6 MHz (JEOL α-500 spectrometer) using D_2O as the external standard. ^{13}C NMR spectra were measured in benzene-d_6 at 25.0 MHz (JEOL FX-100 spectrometer) in the presence of TMS as the internal standard.

Alcohols *1- 4* showed interesting chemical shifts in ^{17}O NMR spectra, in which the higher branching of the terminal γ-methyl group gave abnormally low-field shift to the oxygen atom (Fig. 1). A plot of the ^{17}O chemical shifts vs the number of carbon atoms in alcohols revealed that there are three trends in chemical shifts, classified into groups A-C.

In group A, the chemical shift goes to the lower field linearly starting from methanol to t-butyl alcohol *(1a)* (Fig. 1).[5-8] This trend in the shift is explained by the β-effect known in the ^{13}C NMR spectrum.[9]



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Group B shows a linearly increasing higher field shift of ^{17}O nuclei with an increasing number of γ-methyl groups in less severely crowded alcohols having moderately crowded alkyl substituents such as *1b, 2a,* and *3a* (Fig. 1). This trend in the shift is explained by the high-field shift caused by the γ-methyl group located at the β-position from the oxygen, and may be due to an effect similar to the γ-effect or the high-field shift effect by the γ-carbon atom in the ^{13}C NMR spectrum.[9]

To our surprise, however, in extremely crowded alcohols having more branched γ-methyl groups such as *3d 4c,* and *4d,* in which three bulky alkyl groups like the t-butyl and isopropyl groups are present, the chemical shift of ^{17}O NMR exhibited an abnormally low-field shift that deviated from line B as indicated in line C in Fig. 1. This abnormal low-field shift is appearently due to the molecular crowdedness and the increasing of the γ-methyl groups branching at the β-position.

Since the effect of concentration to this lower field shift in *4c* (2 mol/l - 0.4 mol/l) was found to be very small, the observed abnormal low-field shift in crowded alcohols such as *3d, 4c,* and *4d* is attributable to the intramolecular, and not to the intermolecular interaction. As the long-range shielding effect of remote C-H and C-C bonds in NMR is low and the chemical shift is linearly correlated with the atom's electron density, the observed abnormal lower field shift of the oxygen in highly crowded alcohols (see C line in Fig. 1) indicates that the oxygen atom's electron density is reduced by the intramolecular interaction with the branched γ-methyl group.

One most plausible explanation for this specific steric low-field chemical shift is as follows. Introducing the t-butyl and isopropyl groups to the molecule locates the terminal γ-methyl hydrogen close to the oxygen atom in a rather pseudo-gauche like orientation.[3] This enables the intramolecular through-space attractive gauche-orbital interaction[3] or weak hydrogen bonding interaction[2,10,11] between the oxygen lone pair and the γ-methyl hydrogen, designated as the CH_3 --- O interaction by *5*. By this through-space attractive interaction, the net charge of the interacting oxygen atom diminishes to give rise to the lower total electron density, causing the lower field chemical shift of the ^{17}O NMR spectrum.

The following points are to be added. Another possibility that the molecular twisting at the C-O bond gives rise to the abnormal chemical shift at these atoms in highly crowded alcohols is ruled out, because the chemical shift of the carbon atom of the C-O bond in the crowded alcohols was found to be rather normal.

Van der Waals compression low-field shifts due to the repulsion between the alkyl group and the oxygen atom reported by Boykin et al. in 7-alkylindanones[7,8,12-14] are also considered as the cause of the abnormal low-field ^{17}O chemical shift in the crowded alcohols. However, the ^{1}H NMR chemical shift of the t-butyl hydrogen in *3d and 4c*, which appeared at the normal position (0.90 and 1.09 ppm in benzene-d_6 respectively), suggested that this effect will not be a key factor to cause the abnormal ^{17}O chemical shift in the crowded alcohols. Thus, we conclude that the through-space attractive CH_3 --- O interaction (*5)* causes the abnormal low field ^{17}O chemical shift in crowded alcohols.

It is interesting to note that in contrast to the oxygen, the ^{13}C NMR spectrum of the C-O carbon atom was found to be much less sensitive to the through-space steric attractive interaction effect due to the methyl group branching. Furthermore, comparison of the chemical shifts of the oxygen and carbon atoms of the C-O bond in these alcohols indicated that the less polarized or less polar C-O bond is generated by the through-space attractive gauche-orbital interaction[3] or hydrogen bonding interaction (CH_3 --- O) indicated by *5* in the highly crowded alcohols, that showed the abnormal low-field shift of the oxygen.

In summary, the intramolecular through-space attractive interaction between the γ-methyl hydrogen and the oxygen lone pair, designated as CH_3 --- O in *5*, generates low electron density at the oxygen atom, which gives the abnormally low-field ^{17}O NMR chemical shift, and the less polar C-O bond in extremely crowded aliphatic alcohols.

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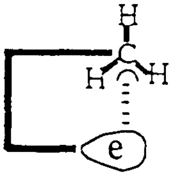

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The through-space attractive gauche-orbital interaction is shown by the conceptual formula (a), in which the dotted line and the designation e represent the gauche-orbital interaction and the lone pair electrons of the heteroatom of the C-X bond, respectively. By this interaction, the electron density changes at e, generating the less polar C-X bond (reverse polarization).

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