Note

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Fumihiko Uchimaru : Studies on N-Substituted Nortropane Derivatives. VI.[1) Intramolecular Hydrogen Bonds of 8-(2-Hydroxyethyl)-3-nortropanone and Related Compounds.

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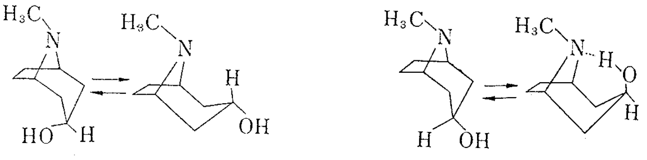
In 1952, Zenitz, *et al.*[2) examined the infrared spectra of tropine (3α-tropanol) (I) and pseudotropine (3β-tropanol) (II) as one of the methods for establishing the configuration of these epimers. As a result, pseudotropine showed more complex and more extensive hydrogen bonding than tropine in dilute carbon disulfide solution and it was concluded that pseudotropine has a *cis* configuration to the N-methyl and hydroxyl groups (Chart 1).



(I) (I′) (II) (II′)

Chart 1.

In this report, the infrared spectral behaviors of 3-(2-hydroxyethyl)-3-nortropanone (III) and related compounds in the same conditions as above are described.

The C=O stretching vibration of (III) in several conditions was determined, comparing with the value of 3-tropanone (IV). As shown in Table I, both (III) and (IV) show a band at 1709 cm^{-1} in liquid film and these data correspond to the values of generally accepted ranges of six-membered ring ketone. In a dilute carbon disulfide solution of 0.007 mole/L., (III) exhibits a band at 1720 cm^{-1} and (IV) at 1718 cm^{-1}, showing no significant differences between the values of these two compounds. Generally, the intermolecular hydrogen bond cannot exist in such a dilute concentration as in the present measurement and, if a carbonyl group forms an intramolecular hydrogen bond, the stretching frequency of this group should shift to a lower side, up to a maximum of 50 cm^{-1}. Consequently, it was presumed that the carbonyl group of (III) does not form a hydrogen bond in this condition. In dilute chloroform solution, (III) and (IV) showed the carbonyl vibrations at 1712 and 1711 cm^{-1}, respectively. This shift is attributed to the solvent effect of chloroform and both compounds exhibit the same behavior.

Table I. $\nu_{C=O}$ of 8-(2-Hydroxyethyl)-3-nortropanone (III) and 3-Tropanone (IV) (cm^{-1}, t=33°C)

Compound	Liquid film	Solution (0.007*M*)	
		CS_2	$CHCl_3$
(III)	1709	1720	1712
(IV)	1709	1718	1711

As for the OH stretching vibrations in dilute carbon disulfide solution, (III) shows a comparatively sharp band at 3610 cm^{-1} and also a more broad band at 3500 cm^{-1}, which

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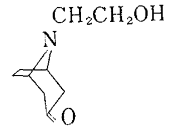
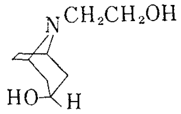
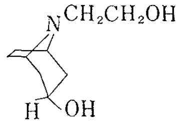
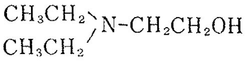
1) Part V : This Bulletin, **10**, 204 (1962).

2) B. L. Zenitz, C. M. Martini, M. Prizner, F. C. Nachod : J. Am. Chem. Soc., **74**, 5564 (1952).

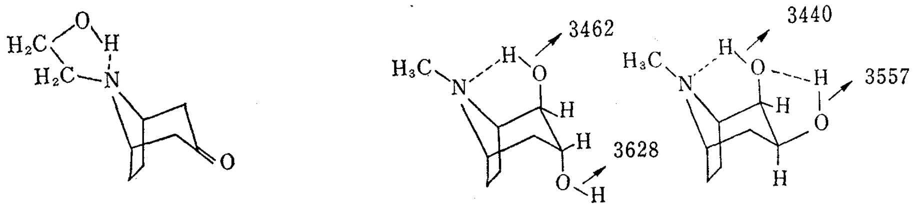
is ascribed to the intramolecular hydrogen bond. If in this circumstance the carbonyl group at C-3 position does not participate in a hydrogen bond, this broad hydrogen bond absorption is considered to arise from an intramolecular hydrogen bond of OH····N type.

To confirm this assumption further, the behavior of OH stretching vibrations of compounds related to (Ⅲ) was also examined, as shown in Table Ⅱ. Two epimers (Ⅴ) and (Ⅵ) obtained by reduction of (Ⅲ) were measured in 0.006 mole/L. carbon disulfide solution. The former showed OH stretching vibrations at 3610 and 3440 cm^{-1}, the latter at 3595 and 3460 cm^{-1}. The intensities of hydrogen bond absorptions at lower frequencies were stronger in (Ⅴ) than in (Ⅵ). The OH····O type hydrogen bond in the molecule of (Ⅴ) is almost impossible, although the same hydrogen bond is conceivable in (Ⅵ) to some extent. Therefore, the existence of intramolecular hydrogen bond in above compounds is confirmed. In addition, a similar compound (Ⅶ) not having a tropane skeleton also shows a broad band at 3460 cm^{-1} in the same condition, which can be ascribed to an intramolecular hydrogen bond. All these data clearly show that the compounds like (Ⅲ), (Ⅴ), (Ⅵ), and (Ⅶ) form intramolecular hydrogen bond of a type OH····N in dilute nonpolar solutions.

Table Ⅱ. ν_{O-H} of 8-(2-Hydroxyethyl)-3-nortropanone (Ⅲ) and Related Compounds (cm^{-1}, t=33°C)

Compound		CS$_2$ Solution (0.007～0.004M)			
		Free O-H	Hydrogen bonded O-H	$\Delta\nu$	Liquid film
	(Ⅲ)	3610	3500	110	3365
	(Ⅴ)	3610	3440	170	3120 (in KBr tablet)
	(Ⅵ)	3595	3460	135	3320
 $\begin{matrix}CH_3CH_2\\CH_3CH_2\end{matrix}\!\!>N-CH_2CH_2OH$	(Ⅶ)	3630	3460	170	3360

Recently, Pinder, *et al.*[3] synthesized two diols (Ⅷ and Ⅸ) possessing a tropane skeleton and measured their OH stretching vibrations in dilute carbon tetrachloride solution. Several absorptions were observed and the structure of intramolecular hydrogen bond was assigned as shown in Chart 2.



(Ⅲ′) *trans*-diol (Ⅷ) *cis*-diol (Ⅸ)

Chart 2.

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3) W. A. M. Davies, J. B. Jones, A. R. Pinder: J. Chem. Soc., **1960**, 3504.

From these values and also from other data,[4] OH····N type intramolecular hydrogen bonded group seems to absorb at lower frequencies than OH····O type hydrogen bonded hydroxyl group. The above data of the present experiment correspond to the values of OH····N type hydrogen bonded hydroxyl groups.

Infrared spectral measurements were carried out by the Hitachi E.P.I. II double-beam spectrophotometer, equipped with an sodium chloride prism. The accuracy of the frequency is assumed to be within ±2 cm^{-1} below 2000 cm^{-1}, and ±10 cm^{-1} over 2000 cm^{-1}. Samples used were all purified by distillation (or chromatography) before use.

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Summary

The infrared spectral behaviors of 8-(2-hydroxyethyl)-3-nortropanone and related compounds in dilute nonpolar solution were examined. From the values of C=O and OH stretching frequencies it was concluded that all these compounds form intramolecular hydrogen bond of a type OH····N. The data obtained also agreed with those of OH····N hydrogen bond appearing in recent literature.

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[4] cf. A. Heusner: Arzneimittel-Forsch., **6**, 105 (1956).