POLISH JOURNAL OF CHEMISTRY
(FORMERLY ROCZNIKI CHEMII)
53, 205 (1979)

INTRAMOLECULAR HYDROGEN BONDS IN β-NITROALCOHOLS. ANALYSIS OF OH STRETCHING BANDS IN THE FIRST OVERTONE REGION *,**

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Analizowano widma absorpcji w podczerwieni drgań rozciągających OH w β-nitroalkoholach w obszarze pierwszych nadtonów. Znaleziono pasma 7100—7090 i 7055—7036 cm^{-1}. Odpowiadają one wolnym i związanym z NO_2 grupom OH. Pasmo 6945 cm^{-1} w 1,3-diolach prawdopodobnie odpowiada grupie OH związanej z inną grupą hydroksylową.

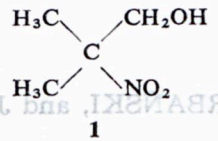
An analysis was made of IR absorption spectra of OH stretching vibration bands of β-nitroalcohols in the first overtone region. Bands at 7100—7090 and 7055—7036 cm^{-1} were recorded. They correspond to OH groups free and bonded with NO_2, respectively. The bands at 6945 cm^{-1} in 1,3-diols probably correspond to a hydroxyl bonded to another hydroxy group.

An intramolecular hydrogen bond between nitro and hydroxyl groups in aliphatic β-nitroalcohols suggested by one of the authors [1] was the subject matter of a number papers [2—16]. Although most of the authors agreed with the existence of the intramolecular hydrogen bond in compounds under consideration, their results differed slightly one from the others and the interpretations were not always sufficiently clear. In view of discrepancies of opinions on this subject, it seemed advisable to take up the studies to dispel the doubts.

The dipole moments examination of some primary β-nitroalcohols was made [17] and the analysis of UV and NMR spectra were also carried out [18]. The results of our studies supported the original hypothesis [1]. We also studied O—H stretching bands of dilute solutions of compounds under consideration in the fundamental region [18]. We observed the presence of bands corresponding probably to the stretching vibrations of hydroxyl groups bonded to nitro groups with intramolecular hydrogen bonds. Since the appearance of these peaks may also be considered as a result of Fermi resonance between the hydroxylic fundamental and a combination band arising from lower-frequency vibrations, we decided

* Chemistry of nitroalkanes. Part CXXXV.
** Dedicated to Professor Osman Achmatowicz on the occasion of his 80th birthday.

to study OH stretching bands in the first overtone region of some of the compounds. We examined the spectra of 2-methyl-2-nitropropane-1-ol (**1**), 2-butyl-2-nitropropane-1,3-diol (**2**), 2,2-dimethylpropane-1,3-diol (**3**), 2-methyl-2-nitro-3-methoxypropane-1-ol (**4**) and compared our results with those for 2-methylpropane-1-ol (**5**) and 2,2-dimethylpropane-1-ol (**6**) published previously [19]. Results are collected in the Table and some of the spectra are presented in the Figure.



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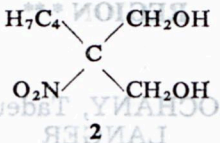

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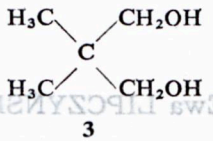

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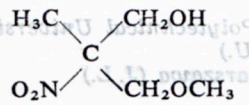

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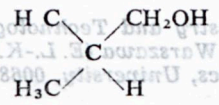

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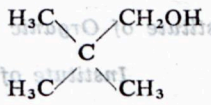

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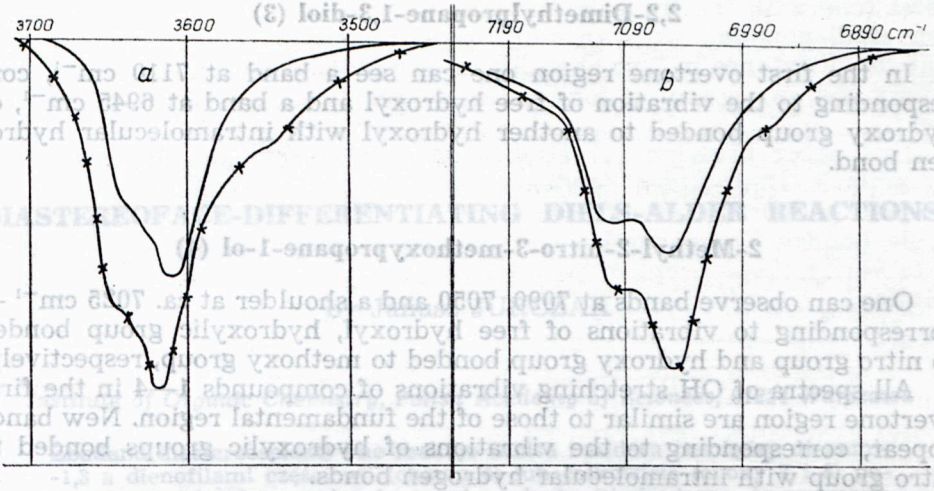
Table

Compound	$\nu_{s(OH)}$, cm^{-1} Fundamental region [18]		First overtone region	
	„free" OH	bonded OH	„free" OH	bonded OH
1	3642 (sh) 3632	3612 —NO_2...HO—	7100	7055 —NO_2...HO—
2	3637 3628 (sh)	3606 —NO_2...HO— 3560 —OH...—OH	7090	7036 —NO_2...HO— 6955 —OH...—OH
3	3642 3632 (sh)	3560 —OH...—OH	7110	6945 —OH...—OH
4	3636 3628 (sh)	3611 —NO_2...HO— 3550 —OH...—OCH_3	7090	7050 —NO_2...HO— 7025 —OH...—OCH_3
5*	3640 3624	—	7115 7084	—
6*	3643 3629	—	7118 7093	—

* Results of previous work of the authors[19].



IR spectra of compounds **1** (————) and **4** (—×—×—): *a* — in the fundamental region of $\nu_{S(OH)}$, *b* — in the first overtone region of $\nu_{S(OH)}$

EXPERIMENTAL

2-Methyl-2-nitropropane-1-ol (**1**) and 2-butyl-2-nitropropane-1,3-diol (**2**) were prepared from corresponding nitroparaffine and formaldehyde by the known procedure [20]. 2,2-Dimethylpropanediol-1,3- (**3**) was obtained from isobutyl aldehyde and formaldehyde [21]. 2-Methyl-2-nitro-methoxypropane-1-ol (**4**) was prepared according to the method described earlier [22].

Spectra in the first overtone region of the stretching vibrations of hydroxyl were taken with a Cary-17 spectrometer. The 5 cm quartz cells were used. Carbon tetrachloride for spectroscopy (Chemapol, Prague, Czechoslovakia) was dried over P_2O_5 and decanted immediately before use. The concentrations of the solutions were ca. 0.005—0.01 mole/dm³.

A useful relation between the overtone and fundamental hydroxyl frequencies is [19]: overtone frequency = 2 × fundamental frequency $-K$. The experimental value of K was between 164 and 182 cm^{-1}. For compounds **5** and **6** the relation is: overtone frequency = 2 × fundamental frequency -165 cm^{-1}.

RESULTS AND DISCUSSION

2-Methyl-2-nitropropane-1-ol (1) and 2-butyl-2-nitropropane-1,3-diol (2)

In spectra of compounds **1** and **2** one can see bands at 7100 and 7090 cm^{-1}, respectively. They correspond to vibrations of free hydroxyl in analogy to the adequate bands of compounds **5** and **6**, in the first overtone region (Table). The bands at $\nu = 7055$ and 7036 cm^{-1} correspond to the bands at 3612 and 3606 cm^{-1}, respectively, observed in the fundamental region. They are bands of hydroxy groups bonded to nitro groups with intramolecular hydrogen bondings. The band at 6945 cm^{-1} observed in the spectrum of **2** is probably the first overtone of that at 3560 cm^{-1} corresponding to the vibrations of hydroxyl bonded to another hydroxy group with intramolecular bond.

2,2-Dimethylpropane-1,3-diol (3)

In the first overtone region one can see a band at 7110 cm^{-1}, corresponding to the vibration of free hydroxyl and a band at 6945 cm^{-1}, of hydroxy group bonded to another hydroxyl with intramolecular hydrogen bond.

2-Methyl-2-nitro-3-methoxypropane-1-ol (4)

One can observe bands at 7090, 7050 and a shoulder at ca. 7025 cm^{-1} — corresponding to vibrations of free hydroxyl, hydroxylic group bonded to nitro group and hydroxy group bonded to methoxy group, respectively.

All spectra of OH stretching vibrations of compounds **1**—**4** in the first overtone region are similar to those of the fundamental region. New bands appear, corresponding to the vibrations of hydroxylic groups bonded to nitro group with intramolecular hydrogen bonds.

Acknowledgment

Our thanks are due to Professor Z. Buczkowski for helpful discussions.

Received August 1st, 1978.

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