

Intramolecular Hydrogen Bond in Some Secondary and Tertiary Aliphatic β -Nitroalcohols*)

by

Ewa LIPCZYŃSKA-KOCHANY, Jan KOCHANY, Tadeusz URBAŃSKI

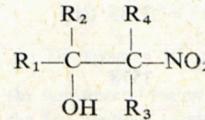
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Summary. The IR spectra of some secondary and tertiary aliphatic β -nitroalcohols have been studied both in the fundamental and the first overtone regions. The new bands at ca. 3575 cm^{-1} have been observed which have been assigned to the stretching vibrations of the hydroxyl groups bonded to the NO_2 groups with an intramolecular hydrogen bond.

In continuation of studies on hydrogen bonds between tertiary nitro and primary alcoholic groups of β -nitroalcohols [1-19] we extended our experiments on the secondary and tertiary aliphatic β -nitroalcohols including also primary and secondary nitro groups. So far the hydrogen bond in these compounds has not been investigated.

Spectroscopic analysis will now be reported in the fundamental region and the first overtones of stretching vibrations of the hydroxyl group.

The nitroalcohols now examined are I-X:



Compound	R_1	R_2	R_3	R_4
I	CH_3	H	H	H
II	$(\text{CH}_3)_3\text{C}$	H	H	H
III	CH_3	H	CH_3	H
IV	CH_3CH_2	H	CH_3	H
V	$(\text{CH}_3)_2\text{CH}$	H	CH_3	H
VI	CH_3	H	CH_3CH_2	H
VII	CH_3CH_2	H	CH_3CH_2	H
VIII	CH_3CH_2	H	CH_3	CH_3
IX	CH_3CH_2	CH_3	H	H
X	CH_3	CH_3	CH_3	H

*) Part CXXI in the series: Chemistry of Nitroparaffins.

Experimental

Nitroalcohols I-X were obtained by the known methods [20-22] by the condensation of corresponding nitroalkanes with suitable aldehydes and ketones in the presence of the catalytic amount of 10 N sodium hydroxide solutions.

Carbon tetrachloride for spectroscopy made by Chemapol (Prague, Czechoslovakia) was dried over P_2O_5 and decanted immediately before use.

The IR spectra in the fundamental region were taken with a Perkin-Elmer PE-577 spectrometer in NaCl cells.

Carbon tetrachloride solutions were made to the concentration of about 0.005 m/l. Sharp peaks, broader peaks and shoulders could be determined to the accuracy of $\pm 1\text{ cm}^{-1}$, $\pm 2\text{ cm}^{-1}$, and $\pm 4\text{ cm}^{-1}$, respectively.

The spectra of the compounds in the same solutions in the first overtone region of $\nu_{\text{S(OH)}}$ were taken with a Cary 17 spectrometer.

The 5 cm quartz cells were used for the measurements.

The data are collected in the Table and typical shapes of the absorption curves of some compounds are given in Figs. 1-4.

An empirical relation between the overtone and the fundamental hydroxyl group frequencies in the Table is:

$$\text{overtone frequency} = 2x \text{ (fundamental frequency)} - 184\text{ cm}^{-1}$$

TABLE

Compound	$\nu_{\text{S(OH)}}$ (cm $^{-1}$)			
	Fundamental region		First overtone region	
	"free" (OH)	bonded (OH)	"free" (OH)	bonded (OH)
Secondary alcohols				
I	3623 (sh) 3603	3585 (sh)	—	—
II	3625 3612 (sh)	3585 (sh)	7066 7040 (sh)	6986 (sh)
III	3622 3605 (sh)	3578	—	—
IV	3625 3602 (sh)	3576	7066 7020	6968
V	3628 3600 (sh)	3570	7072 7016 (sh)	6956
VI	3619 3608 (sh)	3570	—	—
VII	3625 3600 (sh)	3575	7066 7016 (sh)	6950
VIII	3635 (sh) 3612	3575 (sh)	7086 7040 (sh)	6950 (sh)
Tertiary alcohols				
IX	3615	3576	7043	6968
X	3620	3576	—	—

Discussion

Secondary alcohols. All the examined secondary nitroalcohols in solution show two bands (or shoulders) at ca. 3630 cm^{-1} and 3610 cm^{-1} .

This is in agreement with the fact recorded in the literature for all secondary alcohols and assigned to the existence of two conformers with the "free" OH groups [23].

These spectra of nitroalcohols **I** and **II** show the maxima at 3603 cm^{-1} and 3630 cm^{-1} and the shoulders at 3623 cm^{-1} and 3610 cm^{-1} , respectively. They are probably produced by unbonded OH groups. Shoulders at $\nu=3585\text{ cm}^{-1}$ are also present. They should be assigned to the conformers with an intramolecular hydrogen bond between the —OH and —NO₂ groups. The shoulder is more prominent in the spectrum of **I** as compared with that of **II**. This is probably due to the presence of a bulky substituent at the same carbon atom as the hydroxyl group in **II**.

As can be seen from Fig. 1, the spectra of the fundamental and first overtone region are very similar.

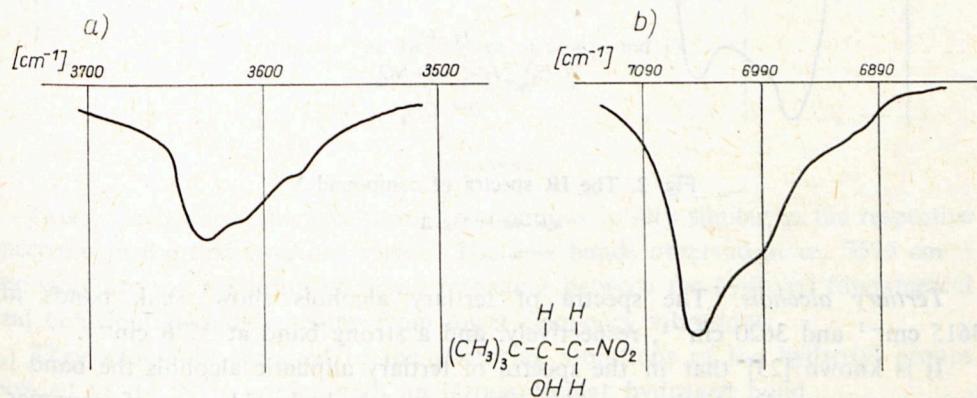
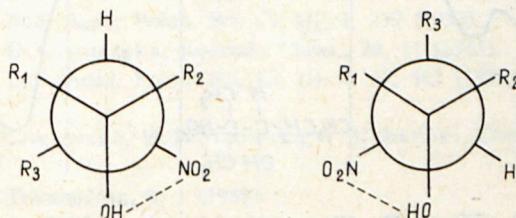


Fig. 1. The IR spectra of compound I

a) in the fundamental region of $\nu_{\text{S(OH)}}$
 b) in the first overtone region of $\nu_{\text{S(OH)}}$

The spectra of nitroalcohols **III–VIII** show the maximum at ca. 3625 cm^{-1} , the shoulder at ca. 3600 cm^{-1} and a visible maximum at 3575 cm^{-1} . All of them can be explained in the same way as for the spectra of compounds **I** and **II**.

In the spectra of compounds **III–VIII** the band (not a shoulder) is present at ca. 3575 cm^{-1} . It seems reasonable to conclude that the presence of one or two



Scheme

alkyl substituents at the carbon atom bonded with the nitro group favours the conformers with an intramolecular hydrogen bond between the $-\text{OH}$ and $-\text{NO}_2$ groups.

This can also be observed in the spectra of the first overtone region of $\nu_{\text{S(OH)}}$ (Figs. 2b, 3b).

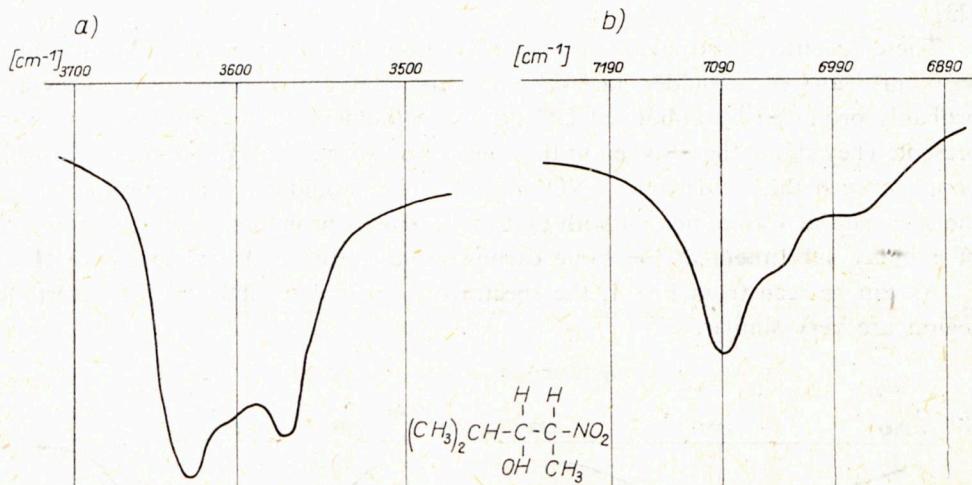


Fig. 2. The IR spectra of compound V

a,b—as in Fig. 1

Tertiary alcohols. The spectra of tertiary alcohols show weak bands at 3615 cm^{-1} and 3620 cm^{-1} , respectively, and a strong band at 3576 cm^{-1} .

It is known [23] that in the spectra of tertiary aliphatic alcohols the band is present corresponding to the stretching vibrations of the hydroxyl group of monomer. That is why the bands at ca. 3615 cm^{-1} in the spectra of **IX** and **X** should be assigned

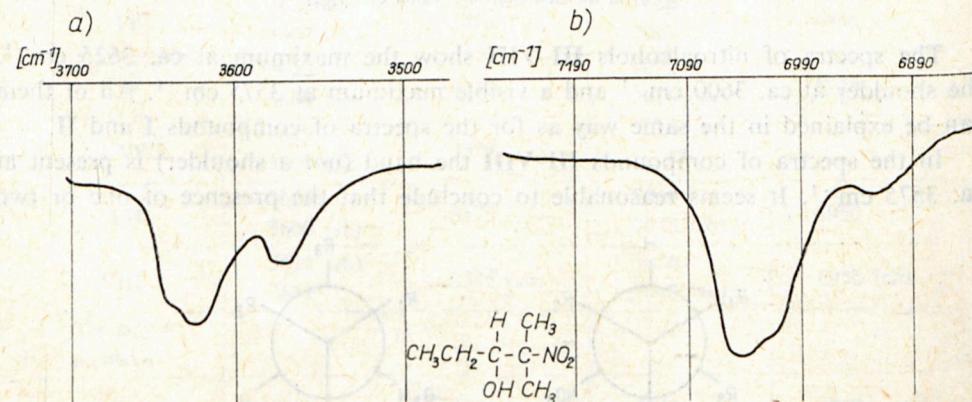


Fig. 3. The IR spectra of compound VIII

a,b—as in Fig. 1

to the unbonded hydroxylic groups. The strong bands at ca. 3576 cm^{-1} are probably produced by the hydroxyl group bonded with the NO_2 group.

The spectra in the fundamental and first overtone region were identical (Fig. 4).

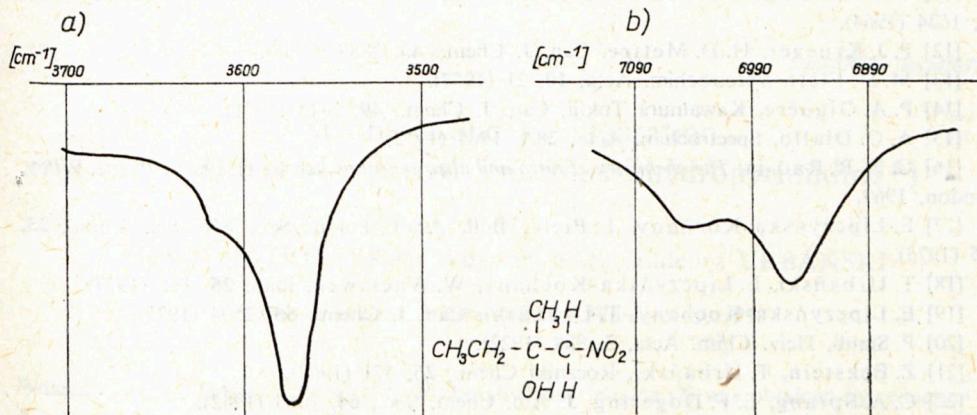


Fig. 4. The IR spectra of compound IX

a,b—as in Fig. 1

Conclusions

Every spectrum of the investigated compounds is very similar to the respective spectrum in the first overtone region. The new bands observed at ca. 3575 cm^{-1} probably are not the result of Fermi resonance between the hydroxyl fundamental and contribution bands arising from lower frequency vibrations.

They should be assigned to the stretching vibrations of the hydroxyl groups bonded to the NO_2 groups with an intramolecular hydrogen bond.

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INSTITUTE OF CHEMISTRY AND ORGANIC TECHNOLOGY, TECHNICAL UNIVERSITY, KOSZY-KOWA 75, 00-662 WARSAW
(INSTYTUT CHEMII I TECHNOLOGII ORGANICZNEJ, POLITECHNIKA WARSZAWSKA)

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Е. Липчиньска-Коханы, Я. Коханы, Т. Урбаньски, Внутримолекулярная водородная связь некоторых вторичных и третичных алифатических β -нитроспиртах

Содержание. Исследованы ИК спектры некоторых вторичных и третичных алифатических β -нитроспиртов. Полученные результаты доказывают присутствие конформеров этих соединений, в которых существует внутримолекулярная водородная связь между нитро- и гидроксильной группами.