ROCZNIKI CHEMII
ANN. SOC. CHIM. POLONORUM
51, 2349 (1977)

CHEMISTRY OF NITROALKANES. PART CXXV *. INTRAMOLECULAR HYDROGEN BONDS BETWEEN OH, OCH_3 AND NO_2 GROUPS

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Zbadano widma IR i H-NMR 2-metylo-2-nitro-3-metoksypropano-1-olu i stwierdzono obecność wewnętrznych wiązań wodorowych między grupami OH i OCH_3 oraz OH i NO_2.

Исследованы спектры ИК и ЯМР 2-метил-2-нитро-3-метокси-1-ол и установлено присутствие внутренных водородных связей между группами OH и OCH_3, а также OH и NO_2.

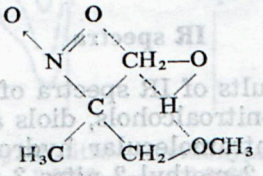
IR and H-NMR spectra of 2-methyl-2-nitro-3-methoxypropane-1-ol were examined. The presence of intramolecular hydrogen bonds was established between OH and OCH_3 as well as OH and NO_2.

An intramolecular hydrogen bond between hydroxylic and nitro groups in aliphatic β-nitroalcohols suggested by Urbański between 1951 and 1959 was examined by many authors [1–16]. As the bond under consideration is weak, there are different opinions about the subject. Thus, it was advisable to collect more information by various methods about the conformational structure of β-nitroalcohols.

A molecule of 2-nitroethanol was investigated by SCF LCAO MO CNDO/2 method to obtain the dipole moments, total energies and charge densities on each atom in a few conformers [17]. The measurement and calculation of dipole moments of some primary β-nitroalcohols [18] were originally chosen to extend the preliminary notes published earlier [5,8]. Analyses of UV, IR and NMR spectra [19] were also carried out. IR spectra in fundamental and first overtone regions of some secondary and tertiary β-nitroalcohols were taken [20].

All our results confirmed the suggestion on existence of an intramolecular hydrogen bond in β-nitroalcohols.

2-Methyl-2-nitro-3-methoxypropane-1-ol seems to be an interesting subject for such an examination as two kinds of intramolecular hydrogen bond can be present, i.e. (1) between OH and NO_2 groups, (2) between OH and oxygen of the methoxy group:



* Part CXXIV: Piotrowska H., Sas W., Urbański T., *Bull. Acad. Polon. Sci., sér. sci. chim.*, in press.

Analysis of IR and NMR spectra of this compound form a subject matter of the present paper. Results are compared with those for β-nitroalcohols [19] and diol ethers obtained by other authors [21–23].

EXPERIMENTAL

Preparation

2-Methyl-2-nitro-3-methoxypropane-1-ol was prepared from nitroethane in four steps: (1) 2-Nitropropane-1-ol was obtained according to the literature [24]. (2) 2-Nitropropyl acetate was prepared according to the known method [25]. (3) 2-Methoxy-2-nitropropane was obtained analogously to the method of Feuer and Markowsky [26] for other nitroalkyl ethers. (4) 2-Methyl-2-nitro-3-methoxypropane-1-ol: the method of Urbański [27] for preparation of nitroalcohols was used. It produced a 75% yield of 2-methyl-2-nitro-3-methoxypropane-1-ol, b.p. 96—97°C/2 mm Hg.

Solvent

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

IR spectra

The spectra of IR absorption within the range of 3400—3700 cm^{-1} were measured with a Perkin-Elmer PE-577 (Perkin Elmer Ltd., 1970, England) spectrometer. Solutions in carbon tetrachloride were made to concentrations 0.0096—0.0221 mole/dm^3. Sharp peaks, broader peaks and shoulders could be determined to an accuracy of ±1, ±2 and ±4 cm^{-1}, respectively.

NMR spectra

NMR data were determined with a 100 MHz Jeol spectrometer in carbon tetrachloride using tetramethylsilane as internal reference. Three series of solutions of various concentrations (0.005—0.030 mole/dm^3) for every temperature (+20° and +65°C) were made up. Values of frequencies were taken from the frequency meter with an accuracy of ±0.05 Hz. The values of chemical shifts of OH proton were extrapolated to infinitive dilution by the method of least squares. The accuracy of the chemical shifts measurements was of the order of 0.3 Hz. The spectral parameters were obtained from the experimental transitions using the iterative procedure of the LAOCOON program [28].

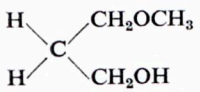
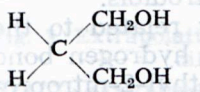
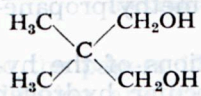
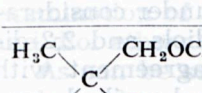
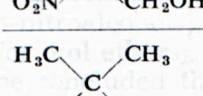
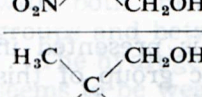
RESULTS AND DISCUSSION

IR spectra

A comparison of the results of IR spectra of the compound under consideration with those for β-nitroalcohols, diols and diol ethers (the Table, Fig. 1) suggests that the intramolecular hydrogen bond between hydroxylic and nitro groups in 2-methyl-2-nitro-3-methoxypropane-1-ol does exist.

Table — Tablica

IR and NMR spectra: wave numbers $\nu_{S(OH)}$ and proton chemical shifts $\delta_{(OH)}$
Widma IR i NMR: liczby falowe $\nu_{S(OH)}$ oraz protonowe przesunięcia chemiczne $\delta_{(OH)}$

Compoud	$\delta_{(OH)}$* (ppm) (TMS)	Ref.	$\nu_{S(OH)}$, cm^{-1}		Ref.
			free	bonded	
Aliphatic alcohols	0.5—0.8	30, 31	3646 3636	—	19
	1.78	23	3640 3641	3547 3554	23 22
	—	—	3641	3554	22
	1.56 —	19 —	3642 3632 3641.7	3560 3553.7	19 21
	1.90 1.80	this paper	3636 3628	3611 3550	this paper
	1.99	19	3640	3612 3632	19
	1.99	19	3636 3628	3606 3560	19

* Values extrapolated to infinite dilution — Wartości ekstrapolowane do rozcieńczenia nieskończenie wielkiego.

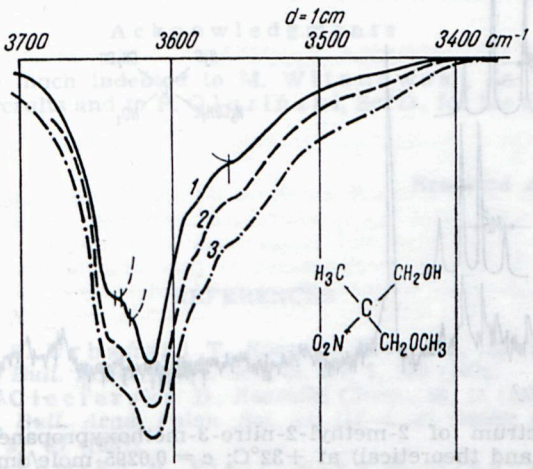
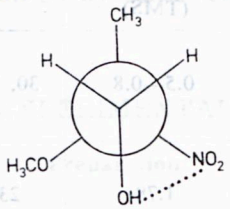


Fig. 1. IR spectra of 2-methyl-2-nitro-3-methoxypropane-1-ol in the $\nu_{S(OH)}$ region. Concentration: ——— 0.0096, - - - - 0.0165, —·—·— 0.0221 mole/dm^3
Rys. 1. Widma IR 2-metylo-2-nitro-3-metoksypropanolu-1 w zakresie drgań $\nu_{S(OH)}$

It seems that gauche is the preferred conformation with hydrogen bond between —NO_2 and —OH groups:



This bond is probably somewhat weaker than that in β-nitrodiols.

The bands at $\nu_S = 3636$ and 3628 cm^{-1} are probably related to the vibrations of the hydroxyl, which does not participate in hydrogen bond (in analogy to the bands at $\nu_S = 3640$, 3632 cm^{-1} of 2-methyl-2-nitropropane-1-ol and the bands at $\nu_S = 3646$, 3636 cm^{-1} of 2-methylpropane-1-ol [19]).

The band at $\nu_S = 3550$ cm^{-1} corresponds to the vibrations of the hydroxy group bonded with the methoxy group. Intramolecular hydrogen bond between —OH and —OCH_3 groups in the compound under consideration is rather stronger than —OH···OH bond in β-nitrodiols and 2,2-dimethylpropane-1,3-diol (the Table). The results are in agreement with those of the IR of the aliphatic diols and diol ethers described previously [21–23].

NMR spectra

The spectrum of the compound under consideration is presented in Fig. 2. We examined proton chemical shift of hydroxylic group of this compound. We studied a dependence of $\delta_{(OH)}$ on concentration analogously

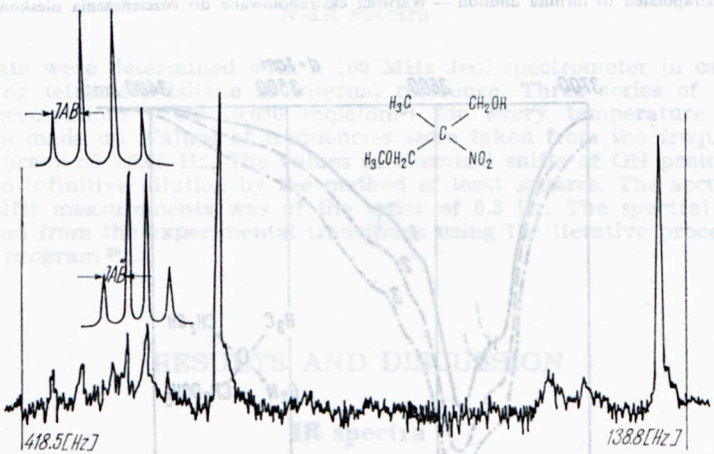


Fig. 2. NMR spectrum of 2-methyl-2-nitro-3-methoxypropane-1-ol (experimental and theoretical) at +32°C; $c = 0.0295$ mole/dm^3

Rys. 2. Widmo NMR 2-metylo-2-nitro-3-metoksypropanolu-1 (doświadczalne i teoretyczne) w temp. +32°; $c = 0{,}0295$ mola/dm^3

$\delta(AB) = 387.0$ Hz, $\delta(A'B') = 371.0$ Hz, $\delta(OCH_3) = 335.0$ Hz, $\delta(CH_3) = 151.0$ Hz, $J(AB) = -12.0$ Hz, $J(A'B') = -10.0$ Hz

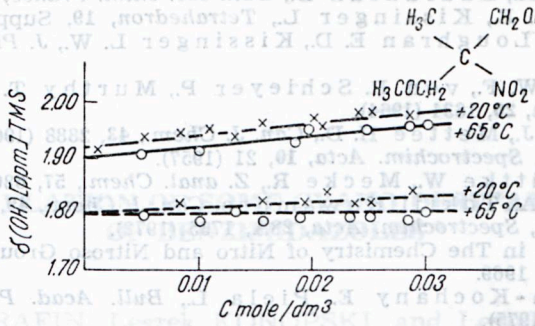


Fig. 3. Extrapolation of $\delta_{(OH)}$ of 2-methyl-2-nitro-3-methoxypropane-1-ol to infinite dilution at temperatures: +20°C (×) and +65°C (○)

Rys. 3. Ekstrapolacja $\delta_{(OH)}$ 2-metylo-2-nitro-3-metoksypropanolu-1 do rozcieńczenia nieskończenie wielkiego w temperaturach: +20° (×) i +65° (○)

to the papers [19,29] (Fig. 3). The results of $\delta_{(OH)}$ extrapolation to the infinite dilution are compared in the Table with our previous results of NMR examination of β-nitroalcohols [19] and with the data for aliphatic alcohols and diol ethers obtained by other authors [23].

As can be seen in the Table, after the dilution, one proton resonance peak tends to reach 1.90 ppm (which is very near to that obtained for β-nitroalcohols), the other one — to $\delta_{(OH)} = 1.80$ ppm (near to that obtained for diol ethers). When comparing the results presented in the Table, it can be concluded that conformers of the compound under consideration exist with both intramolecular hydrogen bonds: between —OH and —NO_2 groups and between —OH and —OCH_3 groups.

The hydrogen bond between —OH and —NO_2 groups ($\delta_{(OH)} = 1.90$ ppm) seems to be weaker than that in β-nitrodiols-1,3 ($\delta_{(OH)} = 1.99$ ppm). As has been mentioned previously, the same conclusion can be drawn from the IR spectra.

Acknowledgments

The authors are much indebted to M. Witanowski, Sc. D., for the useful discussion on NMR results and to P. Gluziński, Sc. D., for his calculation of NMR spectra.

Received April 6th, 1977.

REFERENCES

1. Malinowski S., Urbański T., *Roczniki Chem.*, **25**, 183 (1951).
2. Urbański T., *Bull. Acad. Polon. Sci., cl. III*, **1**, 239 (1953).
3. Urbański T., Ciecierska D., *Roczniki Chem.*, **29**, 11 (1955).
4. Urbański T., *Bull. Acad. Polon. Sci., cl. III*, **4**, 87 (1956); *ibid.*, **4**, 381 (1956); *Roczniki Chem.*, **31**, 37 (1957).
5. Całus H., Jankowska H., Piotrowska H., Urbański T., *Chemistry a. Industry*, **1959**, 1286.
6. Urbański T., *Tetrahedron*, **6**, 1 (1959).
7. Urbański T., in Hydrogen Bonding, Symposium at Ljubljana, 1957, ed. D. Hadži, Oxford 1959, p. 143.

8. Lumbroso H., Lauransan D., *Bull. soc. chim. France*, **1959**, 513.
9. Ungnade H. E., Kissinger L., *Tetrahedron*, **19**, Suppl. 121 (1963); Ungnade H. E., Loughran E. D., Kissinger L. W., *J. Phys. Chem.*, **66**, 2643 (1962).
10. Baitinger W. F., von R. Schleyer P., Murthy T. S. S., Robinson L., *Tetrahedron*, **20**, 1634 (1964).
11. Krueger P. J., Mettee H. D., *Can. J. Chem.*, **43**, 2888 (1965).
12. Flett M. St., *Spectrochim. Acta*, **10**, 21 (1957).
13. Kuhn M., Lüttke W., Mecke R., *Z. anal. Chem.*, **57**, 680 (1963).
14. Giguère P. A., Tokiji Kawamura, *Can. J. Chem.*, **49**, 3815 (1971).
15. Diallo A. O., *Spectrochim. Acta*, **28A**, 1765 (1972).
16. Rao C. N. R., in The Chemistry of Nitro and Nitroso Groups, ed. Feuer H., Part I, London 1969.
17. Lipczyńska-Kochany E., Piela L., *Bull. Acad. Polon. Sci., sér. sci. chim.*, **23**, 895 (1975).
18. Lipczyńska-Kochany E., Urbański T., Wacławek W., *Bull. Acad. Polon. Sci., sér. sci. chim.*, **25**, 185 (1977).
19. Lipczyńska-Kochany E., Urbański T., *Can. J. Chem.*, **55**, 2504 (1977).
20. Lipczyńska-Kochany E., Kochany J., Urbański T., *Bull. Acad. Polon. Sci., sér. sci. chim.*, **25**, 513 (1977).
21. Schleyer P. von R., *J. Am. Chem. Soc.*, **83**, 1368 (1961).
22. Foster A. B., Haines A. H., Stacey M., *Tetrahedron*, **16**, 177 (1961).
23. Saito H., Yonezawa T., Matsuoka S., Fukui K., *Bull. Chem. Soc. Japan*, **39**, 989 (1966).
24. Торф С. Ф., *Мед. Пром. СССР*, **19**, No 7, 26 (1965); *Chem. Abs*, **63**, 11417 g (1965).
25. Shechter H., Shepard J. W., *J. Am. Chem. Soc.*, **76**, 3617 (1954).
26. Feuer H., Markowsky S., *J. Org. Chem.*, **29**, 929 (1964).
27. Urbański T., Chylińska B., *Roczniki Chem.*, **31**, 695 (1957).
28. Bothner-By A. A., Castellano S., *J. Chem. Phys.*, **41**, 3863 (1964).
29. Dąbrowska U., Urbański T., Witanowski M., Stefaniak L., *Roczniki Chem.*, **38**, 1323 (1964).
30. Pople J. A., High Resolution Nuclear Magnetic Resonance, New York 1959.
31. Forsen S., *Svensk. Kem. Tidskr.*, **74**, 139 (1962).

CHEMIA NITROPARAFIN. CXXV. WEWNĘTRZNE WIĄZANIA WODOROWE POMIĘDZY GRUPAMI OH, OCH_3 ORAZ NO_2

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Zbadano widma IR i H-NMR 2-metylo-2-nitro-3-metoksypropanolu-1. Zaobserwowano występowanie pasm $\nu_{S(OH)}$, charakterystycznych dla drgań grup hydroksylowych związanych wewnętrznymi wiązaniami wodorowymi z grupami NO_2 oraz OCH_3. Wyniki badań wpływu rozcieńczania na przesunięcia chemiczne protonu grupy hydroksylowej potwierdzają również obecność wewnętrznych wiązań wodorowych pomiędzy grupami OH i NO_2 oraz OH i OCH_3 w omawianym związku.