BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Série des sciences chimiques
Volume XXVI, No. 6, 1978

ORGANIC CHEMISTRY

Dipole Moments of Some Secondary and Tertiary Aliphatic β-Nitroalcohols and Hydrogen Bond*)

by

Ewa LIPCZYŃSKA-KOCHANY, Jan KOCHANY, Tadeusz URBAŃSKI

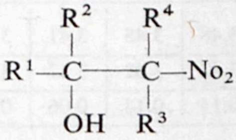
Presented by T. URBAŃSKI on January 14, 1978

Summary. Dipole moments of some secondary and tertiary β-nitroalcohols have been measured. The results were in a good agreement with the previously published examination of these compounds by IR spectroscopy.

An intramolecular hydrogen bond between tertiary nitro and primary hydroxy groups of aliphatic β-nitroalcohols was discussed in a number of papers [1–6].

The results of recently published examination of the IR, NMR and UV spectra [1, 3, 4, 6] and of the dipolometric studies [2], and calculation by the SCF LCAO CNDO method [5] support the hypothesis of the existence of the hydrogen bond in the compounds under consideration.

Further measurements of the dipole moments are the subject of the present paper. They are related to some secondary and tertiary aliphatic β-nitroalcohols **I–VII**:



$$\mathrm{R^1}-\overset{\mathrm{R^2}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{R^4}}{\underset{\mathrm{R^3}}{\mathrm{C}}}-\mathrm{No_2}$$

	R^1	R^2	R^3	R^4
I	CH_3	H	H	H
II	C_2H_5	H	CH_3	H
III	C_2H_5	H	C_2H_5	H
IV	$(CH_3)_2CH$	H	CH_3	H
V	C_2H_5	H	CH_3	CH_3
VI	C_2H_5	CH_3	H	H
VII	$(CH_3)_2CH$	CH_3	H	H
VIII [2]	H	H	CH_3	CH_3

---

*) Part CXXXII in the series: Chemistry of Nitroalkanes.

The dipole moments of compounds **I–VII** were measured in benzene and dioxane in order to find the solvent effect [7]. The results are collected in the Table and compared with those of the dipole moments examinations of 2-methyl-2-nitropropane-1-ol (**VIII**) [2].

Experimental

Nitroalcohols were obtained by known methods [8–10].

Benzene and dioxane were of analytical grade from Merck-Darmstadt and Xenon-Łódź (Poland), respectively. They were purified as described in [1]. Their densities at 20°C were 0.8740 g/cc and 1.0337 g/cc, respectively.

Dielectric constants were measured at 20°C by heterodyne method with a Dipolmeter type DMO1, Weilheim (Federal Republic of Germany) with the DFL-1 cell. The experimental error was of the order $\Delta\varepsilon/\varepsilon = 4\times10^{-5}$.

The refractivities for sodium *D*-line were measured with both the Abbé and precision dipping refractometers, Carl Zeiss, Jena. The experimental error of these measurements was $\Delta\eta/\eta = 2\times10^{-4}$ and 2×10^{-5}, respectively.

The dipole moment values were calculated by the Guggenheim–Smith equation [12] and extrapolated to infinite dilution [13].

Results

The results (Table) show that the hydrogen bond in the 1-nitropropane-2-ol (**I**) is weak and can easily be broken by dissolving in dioxane. The "dioxane effect" (0.2 D) is equal to that observed for primary β-nitroalcohols, as described previously [2] (Table).

TABLE

Experimental dipole moments (in D)

Compound / Solvent	I	II	III	IV	V	VI	VII	VIII [12]
benzene	3.41	3.48	3.48	3.41	3.55	3.58	3.41	3.33
dioxane	3.62	3.62	3.62	3.47	3.60	3.76	3.61	3.53
$\Delta\mu$	0.21	0.14	0.14	0.06	0.05	0.18	0.20	0.20

The "dioxane effect" is smaller for compounds **II** and **III** and can be omitted for **IV** and **V**. This is in a good agreement with the results of our examination of the IR spectra [6].

The lack of the "dioxane effect" in **IV** and **V** supports our previous suggestion [6] that the presence of the alkyl substituents at the carbon atom bonded with the nitro group favours the conformers with an intramolecular hydrogen bond. This bond in **IV** and **V** seems to be strong enough not to be broken by dissolving in dioxane.

However, the hydrogen bond between the $-NO_2$ and $-OH$ groups in the tertiary β-nitroalcohols **VI** and **VII** is weak ($\Delta\mu = 0.2$ D).

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

REFERENCES

[1] E. Lipczyńska-Kochany, T. Urbański, Can. J. Chem., **55**, 2504 (1977).

[2] T. Urbański, E. Lipczyńska-Kochany, W. Wacławek, Bull. Acad. Polon. Sci., Sér. Sci. Chim., **25**, 185 (1977).

[3] E. Lipczyńska-Kochany, T. Urbański, Roczniki Chem., **51**, 2349 (1977).

[4] E. Lipczyńska-Kochany, T. Urbański, J. Langer, J. Pol. Chem., [in press].

[5] E. Lipczyńska-Kochany, L. Piela, Bull. Acad. Polon. Sci., Sér. Sci. Chim., **23**, 895 (1975).

[6] E. Lipczyńska-Kochany, J. Kochany, T. Urbański, ibid., **25**, 513 (1977).

[7] J. Hurwic, W. Wacławek, *Wiązanie wodorowe*, ed. by. L Sobczyk, PWN, Warsaw, 1969, p. 277.

[8] P. Staub, Helv. Chim. Acta, **5**, 888 (1922).

[9] Z. Eckstein, T. Urbański, Roczniki Chem., **26**, 571 (1952).

[10] C. A. Sprang, E. F. Dogering, J. Am. Chem. Soc., **64**, 1063 (1942).

[11] A. I. Vogel, *Practical organic chemistry*, Longmans, London, 1948, Polish ed., PWN, 1964.

[12] E. A. Guggenheim, Trans. Faraday Soc., **45**, 714 (1948); J. Smith, ibid., **46**, 395 (1950).

[13] R. J. W. Le Fervre, H. Vine, J. Chem. Soc., **1937**, 1805.

Э. Липчиньска-Кохань, Я. Кохань, Т. Урбаньски, **Дипольные моменты некоторых вторичных и третичных алифатических β-нитроспиртов и водородная связь**

Содержание. Измерены дипольные моменты некоторых вторичных и третичных β-нитроспиртов. Полученные данные совпадают с результатами ИК-спектроскопических исследований этих соединений.