

Intramolecular Hydrogen Bond in Some β -Nitroalcohols*)

by

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Summary. An attempt was made to find new experimental evidence on the existence of intramolecular hydrogen bond in β -nitroalcohols between the nitro and hydroxylic groups. The positive conclusion is based on the examination of dipole moments.

A hypothesis of the existence of an intramolecular hydrogen bond between the alcoholic and nitro groups in aliphatic β -nitroalcohols was given by Urbański *et al.* [1-7] between 1951 and 1959. The suggestion was based on chemical reactivity. [1], on the UV [2, 3, 6, 7] and IR spectroscopy [4, 7] and on the measurement of dipole moments [5]. The latter substantiated the earlier work of Lumbroso and Lauransan [8].

At first the suggestion was met with sharp criticism [9]. However, a number of later papers [10-16] supported the original hypothesis.

In view of the discrepancies of opinion on the subject it seemed advisable to collect more information on the hydrogen bond in β -nitroalcohols.

Thus, the molecule of 2-nitroethanol-1 was examined by the SCF LCAO MO CNDO/2 method. The result of calculations does not exclude the possibility of hydrogen bond formation [17].

The results of UV, IR and NMR studies of β -nitroalcohols will be published later.

The measurement and calculation of dipole moments, which form the subject of the present paper, were originally chosen to extend the preliminary note published earlier [5].

It is known that the dipole moments are very sensitive function of atom coordinates in the molecules. Hence, the dipole moment calculation could exclude some conformations.

On the basis of the dipole moment studies, Lutsikii *et al.* [18], formulated the criteria for assessing the existence of intramolecular hydrogen bonds, viz.:

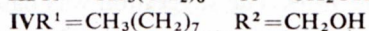
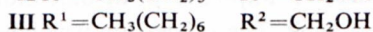
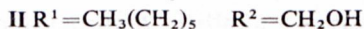
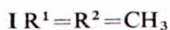
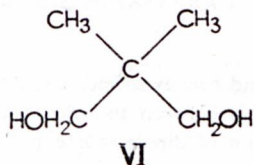
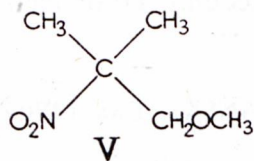
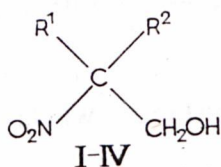
— the lack of "dioxane effect" ;

*) This paper is part CXIV in the series "Chemistry of Nitroalkanes".

— the dipole moments of the alcohols with internal hydrogen bonds are usually much smaller than those of their methyl ethers;

— the measured values of the dipole moments are usually smaller than the values calculated for the free rotation in the compounds.

We have examined 2-methyl-2-nitropropanol-1 (**I**), its methyl ether (**V**), 2-alkyl-2-nitropropane-1,3-diols (**II–IV**) and a diol without the nitro group (**VI**).



The dipole moments of compounds **I–VI** were measured in benzene and dioxane in order to find the solvent effect [18–20], and the dipole moments of various conformers of all compounds were calculated.

The results are collected in Tables I–III.

TABLE I

Experimental dipole moments (in D)

Compound \ Solvent	I	II	III	IV	V	VI
benzene	3.33	3.54	3.52	3.52	3.98	2.70
dioxane	3.53	3.47	3.50	3.58	—	2.50

Experimental

2-Alkyl-2-nitropropane-1,3-diols (**II–IV**) and 2-methyl-2-nitropropanol-1 (**I**) were prepared from corresponding nitroparaffins and formaldehyde by the known procedure [21].

Methyl ether of 2-methyl-2-nitropropanol-1 was obtained by methylation of the alcohol by means of methyl sulphate according to the method described in [22].

2,2-Dimethylpropanediol-1,3 was prepared from isobutyl aldehyde and formaldehyde [23].

Solvents. Benzene and dioxane were of analytical grade from Merck Darmstadt and Xenon-Łódź (Poland), respectively. They were purified by the known method [24]. Their densities at 20°C: 0.8740 g/cc and 1.0337 g/cc, respectively.

Dipole moments measurements. Dielectric constants were measured at 20°C by heterodyne beat method with Dipolmeter type DMO1, Weilheim (Federal Republic of Germany) with DFL-1 cell. The experimental error was of the order of $\Delta\epsilon/\epsilon=4\times 10^{-5}$.

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

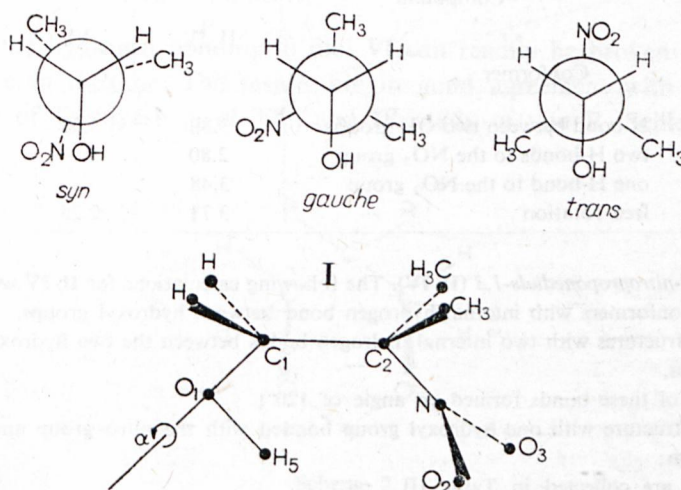
The dipole moment values were calculated by the Guggenheim-Smith equation [25] and extrapolation to infinite dilution [26].

Dipole moments calculations. The Eyring equation [27] was applied to calculate the free rotation of the dipole groups.

The dipole moments of the conformers were calculated according to the Thomson vector model [28].

1. *2-Methyl-2-nitropropanol-1* (I). The dipole moments were calculated for the free rotation of all groups, and also for the *anti*, *gauche* and *syn* conformers.

In the *syn* conformation atoms C_1 , C_2 , O_1 , H_5 and N (I) are lying in one plane (see Scheme 1).



Scheme 1

Calculations were also carried out for the conformer obtained from the *syn* form by rotation of the H_5 proton around the C_1O_1 bond to the angle $\alpha=15^\circ$ in which the distance between H_5 and atom O of the nitro group is the smallest.

TABLE II
Calculated dipole moments of I and V (in D)

Compound	Ia	Ib	Va	Vb
Conformer				
<i>syn</i>	3.13	4.60	3.33	4.40
<i>syn</i> after rotation at 15°	3.10	4.48	—	—
<i>gauche</i>	2.93	4.24	3.19	4.02
<i>anti</i>	2.82	2.82	2.53	2.53
free rotation	3.42		3.28	

The results are collected in Table II and assigned Ia.

The calculations were also done to the conformers which can be obtained by rotation of H_5 around the C_1O_1 bond of the angle $\alpha=180^\circ$ (Ib) (Table II).

2. *Methyl ether of 2-methyl-2-nitropropanol-1* (V). The following calculations were carried out:

— for conformers with the $-OCH_3$ group directed towards $-NO_2$ (Va),

— for the structures with the $-OCH_3$ group deviated from $-NO_2$ (Vb),

— for free rotation of the whole group.

The results are collected in Table II.

3. *2,2-Dimethylpropanediol-1,3* (VI). The dipole moments of the conformers with internal hydrogen bond and of those with free rotation of the groups were calculated. The results are collected in Table III.

TABLE III

Calculated dipole moments of II–IV and VI (in D)

Compound Conformer	II–IV	VI
H-bond between two OH groups	3.80	3.08
two H-bonds to the NO_2 group	2.80	—
one H-bond to the NO_2 group	3.48	—
free rotation	3.71	2.26

4. *2-Alkyl-2-nitropropanediols-1,3* (II–IV). The following calculations for II–IV were done:

— for the conformers with internal hydrogen bond between hydroxyl groups,

— for the structures with two internal hydrogen bonds between the two hydroxyl groups and the nitro groups.

The planes of these bonds formed an angle of 120° ;

— for the structure with one hydroxyl group bonded with the nitro group and the other of the free rotation;

The results are collected in Table III.

Discussion

A comparison of the experimental data with results of calculations

2-Methyl-2-nitropropanol-1 (I). As can be seen from Table II, conformations Ib can be excluded since they give much higher μ values than the experimental ones. The excluded conformations do not correspond to the hydrogen bond formation. All other conformers except the *anti* conformation, could correspond to the intramolecular hydrogen bond.

It should be pointed out that the same conclusions follow from the dipole moments calculations of 2-nitroethanol-1 by the CNDO/2 method [17].

The values of the dipole moment of nitroalcohol I measured in benzene (3.3 D) is lower than that of its methyl ether (3.98 D). This fact supported the theory of the existence of hydrogen bonding in nitroalcohol I.

On the other hand, the difference between the $\mu_{I\text{exp}}$ values in benzene and $\mu_{I\text{free rotation}}$ is very small (0.10 D) and the distinct "dioxane effect" can be observed. ($\mu=0.2$ D).

It follows that the intramolecular hydrogen bond in β -nitroalcohol (**I**) is weak and easy to break by dissolving in dioxane.

Methyl ether of 2-methyl-2-nitropropanol-1 (**V**). The experimental value of the dipole moment of ether **V** is considerably higher than those with free rotation and for isomers with the $-\text{OCH}_3$ group directed towards the nitro group.

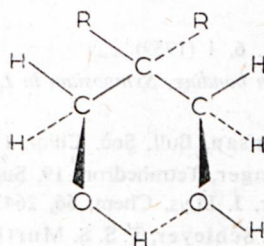
It follows that the examined solutions contained several conformers in equilibrium while the $-\text{OCH}_3$ group deviates from the nitro groups.

2,2-Dimethylpropanediol-1,3 (**VI**). It follows from our dipole moments measurements that among the conformers of compounds **VI** there exists a conformer with an intramolecular hydrogen bond between two hydroxyl groups.

The distinct dioxane effect:

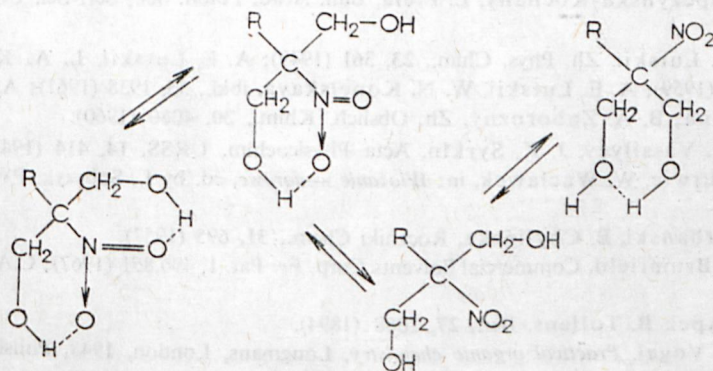
$$\mu_{\text{dioxane}} - \mu_{\text{free rot}} = 2.50 - 2.26 = 0.24 \text{ D}$$

proves that the hydrogen bonding in diol **VI** can readily be broken by dissolving the substance in dioxane. The results are in good agreement with dipolometric investigation of Toshiyasu *et al.* [29] and IR study of von R. Schleyer [30] (see Scheme 2).



Scheme 2

2-Alkyl-2-nitropropanediols-1,3 (**II-IV**). The values of the dipole moments of these compounds are identical irrespectively of whether they were measured in benzene or dioxane. The hydrogen bond in those compounds seems to be sufficiently strong



Scheme 3

not to be broken by dissolving in dioxane. The lack of the "dioxane effect" may suggest the hydrogen bonding between two hydroxyl groups and the nitro group.

However, the dipole moments measured in benzene are nearer to those calculated for the isomer with one internal hydrogen bond $\text{—NO}_2\text{...HO—}$ and the other —OH group unbended. This seems to indicate an equilibrium according to Scheme 3.

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Т. Урбаньски, Е. Липчиньска-Коханы, В. Вацлавек, **Внутримолекулярная водородная связь в некоторых β -нитроспиртах**

Содержание. Исследованы дипольные моменты некоторых β -нитроспиртов. Полученные результаты доказывают присутствие внутримолекулярной водородной связи между нитро- и гидроксильной группами.