BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. IV, No. 2, 1956

CHEMISTRY

On Hydrogen Bonds in Some Nitroalcohols, (on the Basis of Infra-red Absorption Spectra)

by

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Communicated at the meeting of November 28, 1955

The author formerly expressed the view that there exist intramolecular hydrogen bonds between the nitrogroup and the hydroxyl group (or groups) present in nitroalcohols, which can be formed by adding formaldehyde to nitroparaffins.

This was originally based on the difficulty of forming acetals and katals by some nitrodiols [1] and later on by examination of ultraviolet absorption spectra of a larger number of nitroparaffins and their derivatives [2].

Infra-red absorption spectra of a few nitroparaffins and their derivatives — nitroalcohols in the form of suspension in paraffin-oil — have now been examined by J. Świętosławska, T. Kraczkiewicz and B. Kontnik (Institute of General Chemistry, Warsaw).

The results obtained are tabulated below. Some typical absorption curves are also reproduced (Figs. 1-6). For purposes of comparison, pentaerythritol (X) (Fig. 7) was examined.

Analysis of the figures leads to the following conclusions:

(1) The very weak band n_1 near to 7000 cm.$^{-1}$ is present only in those compounds which contain the OH group, or groups.

Repeated measurements confirmed the existence of that band.

According to Ellis and Bath [3], the weak band at 1.44 μ (i. e., 7000 cm.$^{-1}$) in cellulose corresponds to the hydroxyl groups. Nikitin [4] found that bands 1.48 μ and 2.09 μ (i. e., 6757 cm.$^{-1}$ and 4785 cm.$^{-1}$ respectively) in low nitrated (7.6% N) nitrocellulose could be attributed to hydrogen bonds.

In the light of these observations we think it probable that band n_1 is produced by the hydroxyl groups in compounds II, III, V, VI, VIII, IX and X.

(2) The weak band, n_2, is probably formed by the addition of bands of lower frequencies, such as n_3, one of the bands $n_9 - n_{12}$, and one with

a frequency lower than 1000 cm.$^{-1}$. The latter was not investigated in our experiments.

(3) Band n_3 is probably formed by the addition of bands n_7, n_9, e. g. for compound VII,

$$n_3 = 4545,\ n_7 + n_9 = 4505;$$

for compound IX,

$$n_3 = 4444,\ n_7 + n_9 = 4449.$$

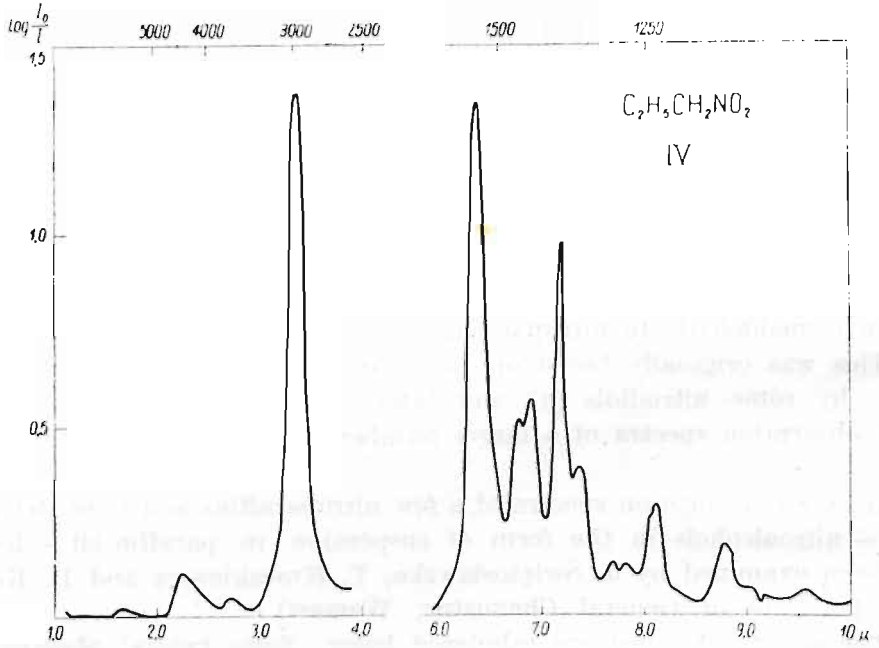
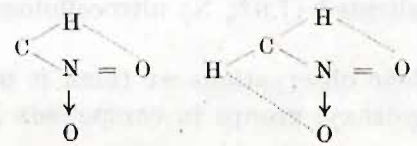


Fig. 1

(4) Band n_4 and n_5 (4167 and 3704 cm.$^{-1}$ respectively) correspond probably to the bonds between carbon and active hydrogen C—H and $C\begin{smallmatrix}H\\H\end{smallmatrix}$ in secondary and primary nitrocompounds.

It seems that structures (A) with hydrogen bonds between the active hydrogen atom and nitrogroup should be considered. This would be a structure intermediate between the tautomeric forms, normal and *aci*:

(A)



The existence of a hydrogen bond would account for the relative weakness of bands n_4 and n_5.

(5) Band n_6 (3448 or 3333 cm.$^{-1}$) is produced by the hydroxyl groups. According to Rodebush [5], the free OH group gives a frequency of 3640 cm.$^{-1}$ and the bonded OH group a frequency of 3330 cm.$^{-1}$. The latter frequency is near to that of n_6.

A large number of experiments on the infra-red spectra of glycols were carried out by L. P. Kuhn [6]. The data thus obtained led him to

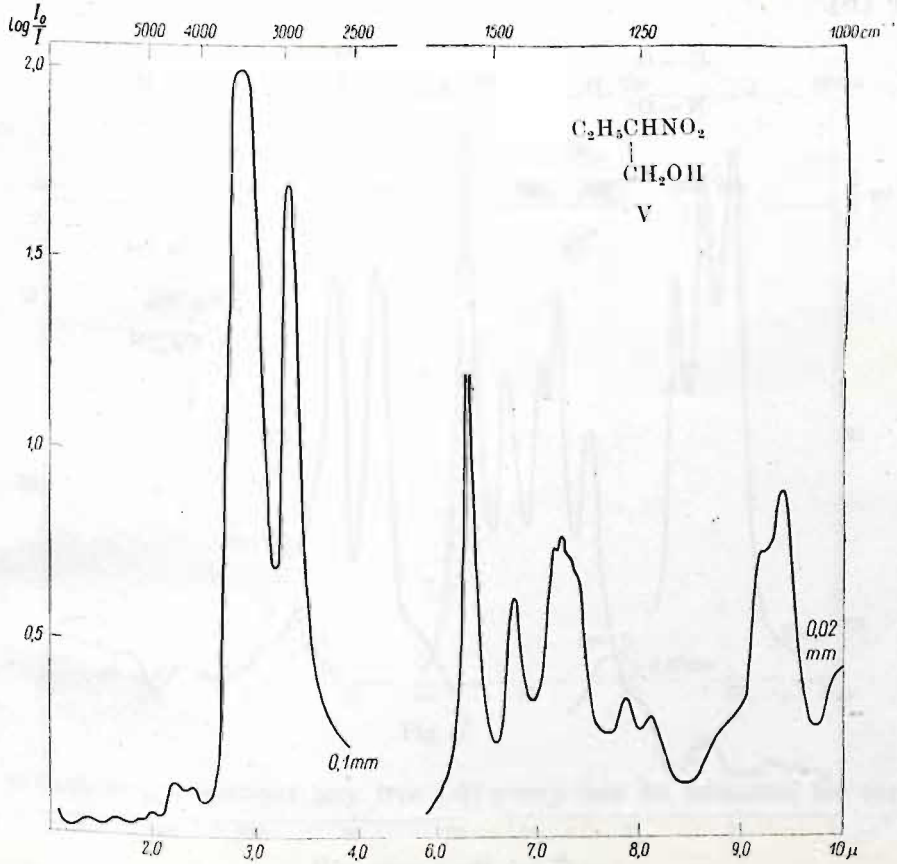
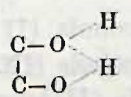


Fig. 2

the conclusion that glycols possess a structure (B), formerly postulated by Davies [7] for pyrocatechol:

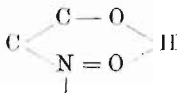
(B)

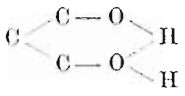


The following fact discovered by Kuhn lends support to this view, viz., that the glycols give two absorption bands, if the length of the hydrogen bond (according to the structure B) is less than 3.3 Å. One of these bands is produced by the free OH group (frequency 3600—3644 cm.$^{-1}$), the other one — by the bonded OH group (frequency 3448—3612 cm.$^{-1}$).

The bonded OH group produces a relatively strong absorption band. In addition, at high concentration or in a solid state, still lower frequencies produced by intermolecular hydrogen bonds may appear.

In our instance two possible structures with intramolecular hydrogen bonds can be postulated: structure (C), which has previously been indicated by the author [2] and structure (D) analogous to Kuhn's structure (B).

(C) 

(D) 

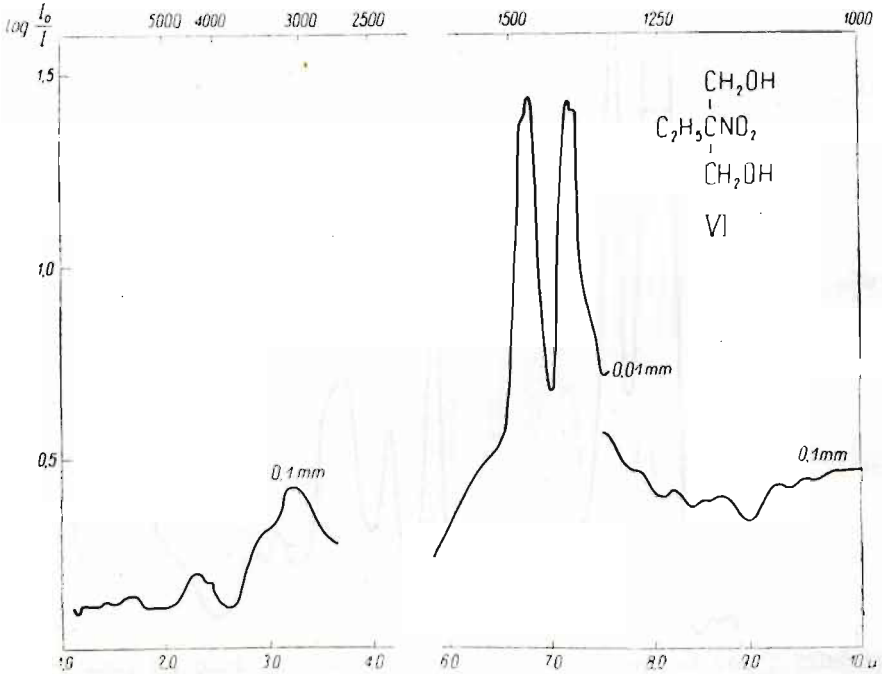


Fig. 3

Also, intermolecular hydrogen bonds should be admitted. They might produce the shifting of the OH bands towards still lower frequencies.

In the monohydric nitroalcohols (II and V) band n_6 is very strong, whereas in the polyhydroxyl alcohols (IX), (X) the band is much weaker and broader, and in the glycols (III) and (VI) it is in the form merely of a bend. A very weak bend n_6 is also observed in compound (VIII) which contains only one OH group.

It is already known in the literature, that bonded hydroxyl groups are often broader than unbonded and the breadth of certain bonded OH bands can be correlated to the strength of the hydrogen bond [6], [8]—[11].

The postulated structures (C) and (D), with two kinds of hydrogen bonds, in compounds (III), (VI), (IX) and (X) are thus in agreement with the already mentioned effect of the decrease in the intensity and broadening of the OH band.

No free hydroxyl groups are present in these compounds and that is probably the reason why no double maxima were noticed for hydroxyl (as found by L. P. Kuhn *)).

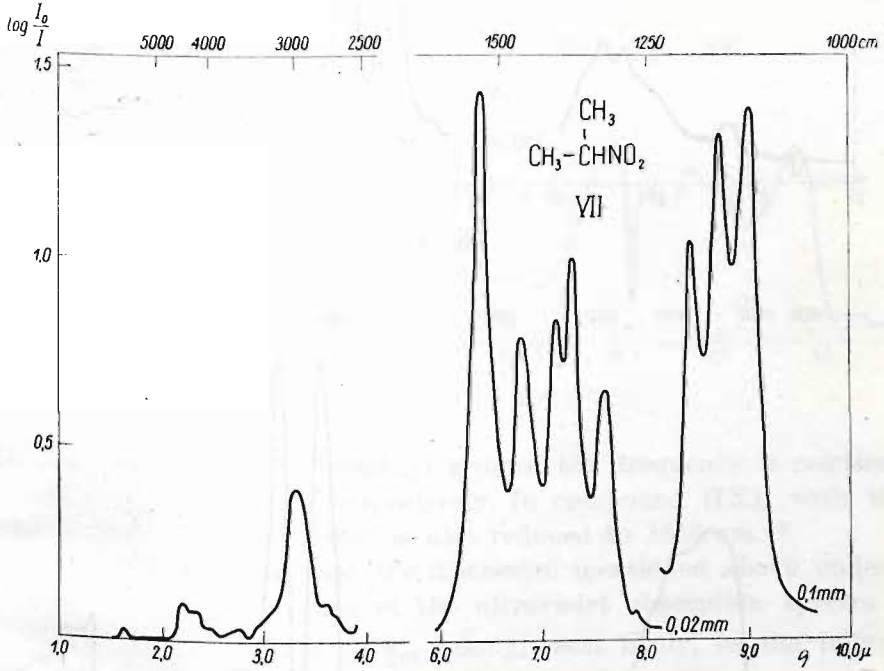
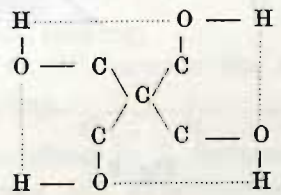


Fig. 4

Structure (E) without any free OH group can be admitted for compound (X).

E)



In monohydroxyl compounds a single hydrogen bond of type (C) without bond (D) should also produce a decrease in the intensity and a broadening of the OH band. This is the case as regards compound (VIII). However, the other two compounds of that type – (II) and (V) –

*) We have confirmed the result arrived at by Kuhn, viz., that OH groups in ethylene glycol give two maxima.

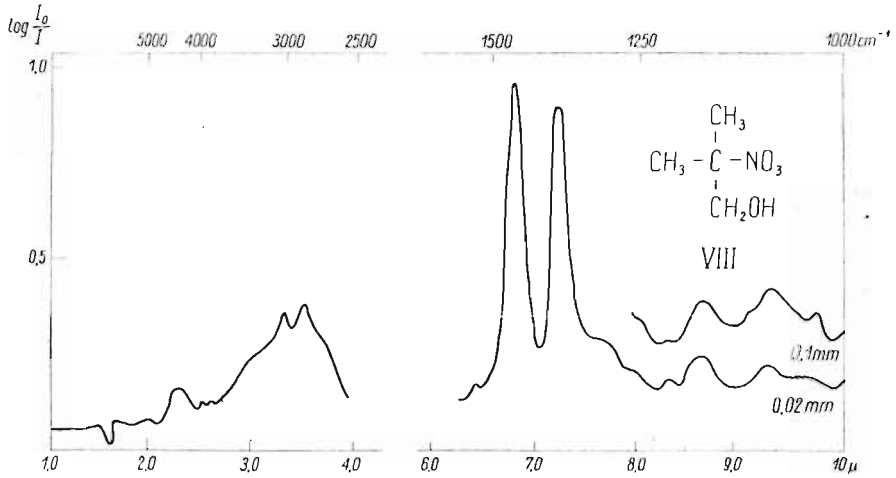


Fig. 5

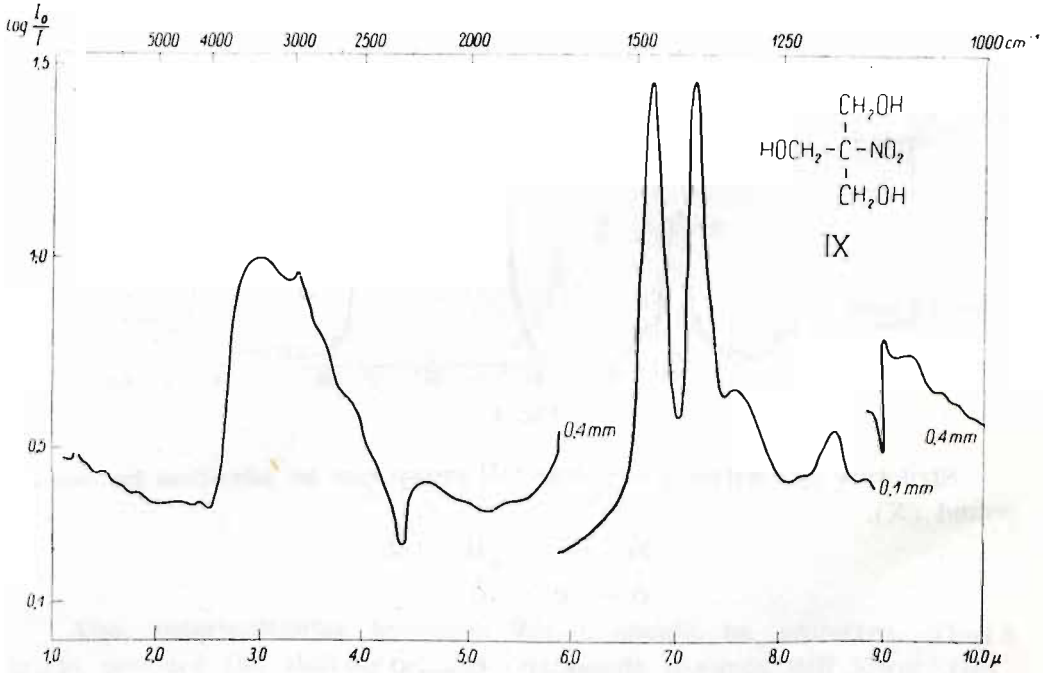


Fig. 6

produce a strong OH band. It is possible to explain this by the presence of the active hydrogen atoms in both compounds. The active hydrogens would form a bond of type (A), which might weaken the bond shown on diagram (C).

The frequency of the NO_2 band (ν_8) of compounds (II) and (V) should not, therefore, differ very much from the frequency of the unbonded NO_2 group, which is actually the case.

(6) The frequency n_7 near 3000 cm.$^{-1}$ corresponds probably to CH_3 or CH_2 stretching vibrations.

(7) Band n_8 is typical for the nitrogroup. In compounds (I), (IV) and (VII), where OH groups are absent, the frequency is 1567 cm.$^{-1}$. The same appears in compounds (II), (V) where only one hydroxyl group and active hydrogen atom are present. In compound (VIII), with one hydroxyl group without an active hydrogen atom and in compounds

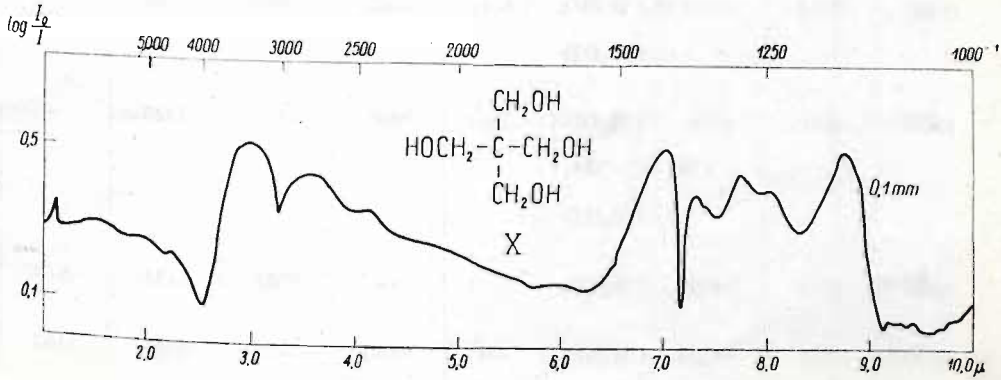


Fig. 7

(III), and (VI), with two hydroxyl groups, the frequency is reduced to 1555 cm.$^{-1}$ and 1543 cm.$^{-1}$ respectively. In compound (IX), with three hydroxyl groups, the frequency is also reduced to 1555 cm.$^{-1}$.

This is in agreement with the discussion mentioned above under (5) and with the former analysis of the ultraviolet absorption spectra [2].

(8) The bands from n_9 to n_{13} belong, most likely, to the following vibrations:

n_9 CH_2 bending,
n_{10} CH_2 wagging,
n_{11} CH_2 twisting,
n_{12} CH_3 or C – C rocking,
n_{13} the bond C – N between the carbon atom and the nitrogen atom of the nitrogroup.

The author is much indebted to J. Świętosławska, B. Kontnik and T. Kraczkiewicz for carrying out experiments of infra-red absorption spectra and to W. Sobótka for preparing the pure substances.

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Frequency of infra-red

No./Figure	Formulae	n_1	n_2	n_3	n_4
I/—	$CH_3CH_2NO_2$	—	6250	4545	—
II/—	$CH_3CH(NO_2)CH_2OH$	7143	6250	4545	4167
III/—	$CH_3C(NO_2)(CH_2OH)_2$	6897	6250	4545	—
IV/1	$C_2H_5CH_2NO_2$	—	6061	4444	—
V/2	$C_2H_5CH(NO_2)CH_2OH$	6897	6061	4545	4167
VI/3	$C_2H_5C(NO_2)(CH_2OH)_2$	6897	6061	4444	—
VII/4	$CH_3CH(CH_3)NO_2$	—	6250	4545	—
VIII/5	$CH_3C(CH_3)(NO_2)CH_2OH$	6993	6061	4444	—
IX/6	$HOCH_2C(NO_2)(CH_2OH)_2$	6897	6061	4444	—
X 7	$HOCH_2C(CH_2OH)_2CH_2OH$	7143	6061	4545	—

absorption bands ν cm.$^{-1}$

Bands								
n_5	n_6	n_7	n_8	n_9	n_{10}	n_{11}	n_{12}	n_{13}
3704	—	3030	1567	1453	1412	1253	1136	1105
—	3448	3030	1567	1464	1374	1245	1117	1070
—	(3448) *)	3030	1543	1464	1383	1245	1130	1081
3704	—	3030	1567	1464	1393	1245	1136	1042
—	3448	2985	1567	1464	1383	1245	1130	1058
—	(3448) *)	3125	1543	1464	1383	1208	1143	1075
3704	—	3030	1567	1475	1374	1186	1143	1099
—	(3448) *)	2944	1555	1464	1383	1208	1156	1075
—	3333	2985	1555	1464	1393	1215	1156	1099
—	3333	2899	—	1464	1412	1238	1136	—

*) A bend

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