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*CHEMISTRY*

# On Hydrogen Bonds in Some Nitroalcohols. II. Infra-Red Absorption Bands of Nitrogroups

by

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In the first paper on infra-red absorption spectra of some nitroalcohols [1] the former hypothesis on hydrogen bonds between the nitrogroup and hydroxyl groups [2] was subjected to a more detailed exa-

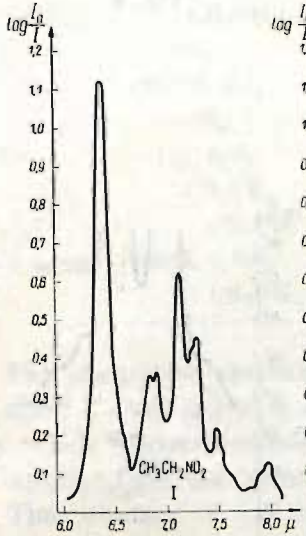



Fig. 1

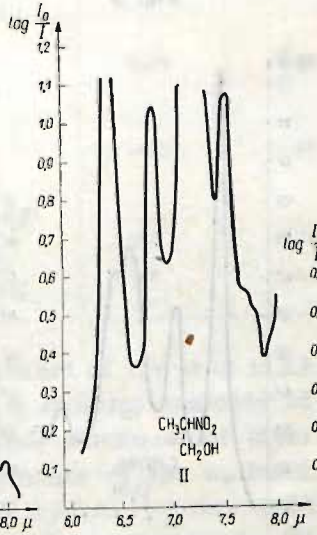



Fig. 2

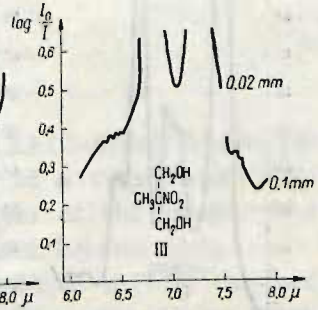



Fig. 3

mination, mainly on the basis of the frequency and intensity of absorption bands produced by the hydroxyl groups.

In the present paper, the $n_8$ absorption band (see [1]), near 6.4 $\mu$, is examined in a more detailed manner, and the $n'_8$ band, near 7.5 $\mu$ (not described in the first paper) is also subjected to consideration.

Figures 1-9 give the absorption curves for the range between c. 6 and 8 $\mu$.

In the compounds (I) (nitroethane), (II) (2-nitropropanol), (IV) (1-nitropropane), (V) (2-nitrobutanol) and (VII) (2-nitropropane), i. e. nitroparaffins or monohydroxylic alcohols with active hydrogen atom atta-

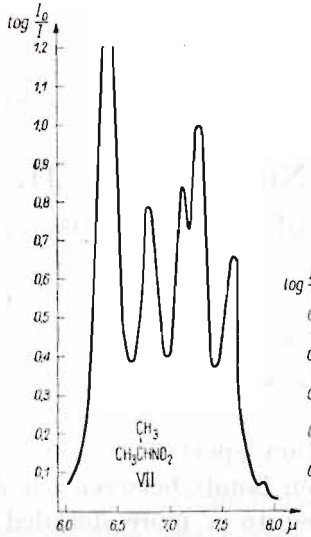



Fig. 4

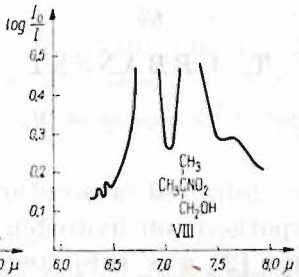



Fig. 5

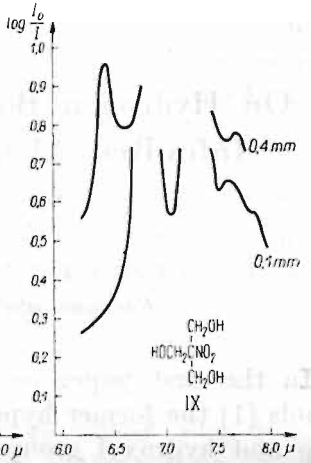



Fig. 6

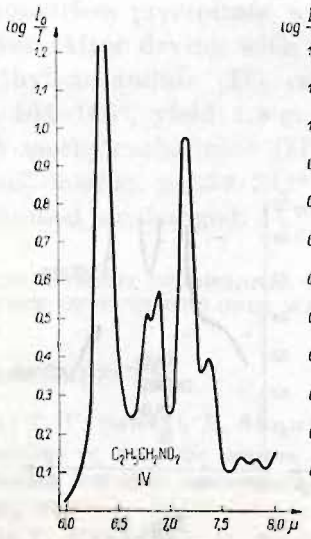



Fig. 7

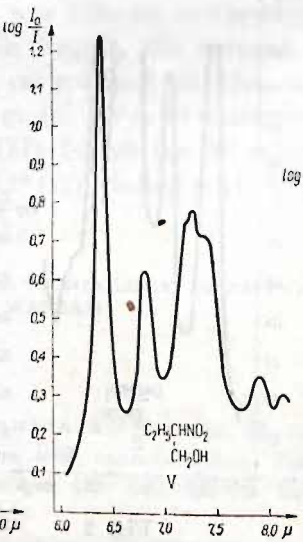



Fig. 8

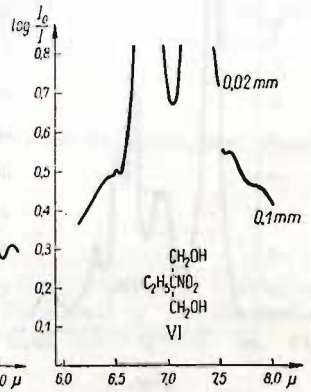



Fig. 9

ched to the carbon atom bonded with the nitrogroup, the frequency is 1567 cm.$^{-1}$. In the alcohols with two hydroxyl groups, i. e. (III) (2-nitro-2-methylpropane-1,3-diol) and (VI) (2-nitro-2-ethylpropane-1,3-diol) or in the alcohol with one hydroxyl group and no active hydrogen attached to the carbon atom bonded with the nitrogroup, i. e. (VIII) (2-nitro-2-methylpropanol), the intensity of the $n_s$ band is very small, the band

becomes broader and the frequency lower: 1543, 1534 and 1555 cm.$^{-1}$ respectively (see Table I).

TABLE I ($n_8$ Band)
Suspension in paraffin-oil

| Number | Formula | Thickness of the layer mm. | $n_8$ Band | | |
|---|---|---|---|---|---|
| | | | Wave length $\mu$ | Frequency cm$^{-1}$. | $\log \frac{I_0}{I}$ |
| (I) | $CH_3CH_2NO_2$ | 0.02 | 6.38 | 1567 | 1.131 |
| (II) | $CH_3CH(NO_2)CH_2OH$ | 0.02 | 6.38 | 1567 | 1.420 |
| (III) | $CH(CH_2OH)_2C NO_2$ | 0.02 | 6.48 | 1543 | 0.383 |
| (IV) | $C_2H_5CH_2NO_2$ | 0.02 | 6.38 | 1567 | 1.337 |
| (V) | $C_2H_5CH(NO_2)CH_2OH$ | 0.02 | 6.38 | 1567 | 1.244 |
| (VI) | $C_2H_5C(CH_2OH)_2 NO_2$ | 0.02 | 6.52 | 1534 | 0.494 |
| (VII) | $CH_3CH(CH_3)NO_2$ | 0.02 | 6.38 | 1567 | 1.444 |
| (VIII) | $CH_3C(CH_3)(CH_2OH)NO_2$ | 0.02 | 6.43 | 1555 | 0.174 |
| (IX) | $HOCH_2C(CH_2OH)_2NO_2$ | 0.1 | 6.43 | 1555 | 0.350 |
| | | 0.4 | „ | „ | 0.975 |

The absorption spectrum of the triol (IX) (2-nitro-2-hydroxymethyl-propane-1,3-diol) gives a striking example of a very weak $NO_2$ band. Only when a considerable thickness of layer of the sample (0.4 mm.) was applied, did the presence of the $n_8$ band become clear.

The presence of one hydroxyl group reduced slightly the frequency of the $n_8'$ band in all examined compounds. Thus, by passing from nitroethane (I) to the corresponding monohydroxylic alcohol (II), $\Delta\nu$ was 9 cm.$^{-1}$. In the instance of 1-nitropropane (IV) or 2-nitropropane (VII) and the alcohols (V) or (VIII) respectively, the decrease of the frequency $\Delta\nu$ was 6 and 5 cm.$^{-1}$ respectively. There was no decrease of the intensity of the absorption, on the contrary — an increase of the intensity of the absorption was noticed.

The presence of two hydroxyl groups markedly reduced the frequency of the band. Thus, the difference between the $n_8'$ frequencies in

TABLE II ($n'_8$ Band)

Suspension in paraffin-oil

| Number | Thickness of the layer mm. | $n'_8$ Band | | |
|---|---|---|---|---|
| | | Wave length $\mu$ | Frequency cm.$^{-1}$ | $\log \frac{I_0}{I}$ |
| (I) | 0.02 | 7.45 | 1342 | 0.208 |
| (II) | 0.02 | 7.50 | 1333 | 1.066 |
| (III) | 0.1 | 7.63 | 1310 | 0.329 |
| (IV) | 0.02 | 7.35 | 1361 | 0.396 |
| (V) | 0.02 | 7.38 | 1355 | 0.719 |
| (VI) | 0.1 | 7.58 | 1319 | 0.554 |
| (VII) | 0.02 | 7.60 | 1316 | 0.664 |
| (VIII) | 0.02 | 7.63 | 1311 | 0.294 |
| (IX) | 0.1 | 7.58 | 1319 | 0.654 |
| | 0.4 | 7.63 | 1311 | 0.783 |

compounds (I) and (III), (IV) and (VI) was 32 and 42 cm.$^{-1}$ respectively. At the same time, intensity of the band considerably decreased and, for a better measurement, a thicker layer of the suspension had to be applied.

The same low frequency of the $n'_8$ band (1311-1319 cm.$^{-1}$) was noticed with compound (IX) containing three hydroxylic groups, the intensity of the absorption being also relatively small.

## Discussion

It was formerly noticed that the maximum of ultraviolet absorption near 270 $m\mu$ due to $NO_2$ group was transformed into a more or less pronounced band under the influence of two hydroxyl groups. This was explained by the formation of six-membered chelate rings, containing hydrogen bonds between OH groups and the $NO_2$ group [2], according to diagramm (C). Further support to this hypothesis was given by the examination of the frequencies and intensities of OH bands in the infrared absorption spectrum [1], and the experimental facts described in the present paper seem to confirm this view.

Here are the main points in favour of the hypothesis on hydrogen bonds between OH and $NO_2$ groups (in addition to those mentioned in the first publication [1]):

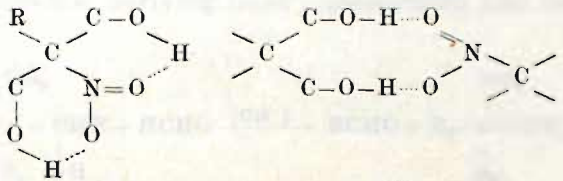
1. The frequency and intensity of the $n_8$ and $n'_8$ bands are considerably reduced in presence of at least two hydroxyl groups.

2. One hydroxyl group slightly reduces the frequency of the $n'_8$ band and in the compounds (II) and (V) no decrease of the intensity of the bands has been noticed.

3. One hydroxyl group without an active hydrogen atom attached to the carbon bonded with the nitrogroup (compound VIII), reduces the frequency and intensity of the $n_s$ band. The intensity of the $n_s'$ band is also considerably reduced.

It remains unexplained why in compound (VIII) one hydroxyl group produced such a strong effect upon the intensity of the $n_s$ band, whereas in the compounds (II) and (V) no lowering of the intensity of the $n_s$ band was noticed. The only explanation we can give for the time being, is based on the difference between the structure of the compound (VIII) on one side and the compounds (II) and (V) on the other. The former does not contain, while the two latter compounds contain the active hydrogen atom attached to the carbon atom bearing the nitrogroup. The active hydrogen either weakens the hydrogen bonds of type (C) (as it was admitted in the previous paper [1]), or increases the intensity of $NO_2$-vibrations.

It seems also that the substances in solid form possess another kind of hydrogen bonds between the OH and the $NO_2$ groups, in addition to the bonds according to (C). This would be the intermolecular bonds of the type (F).



(C) (F)

The (F) bonds would increase the effect of the (C) bonds upon the infra-red absorption spectrum. In order to establish the correctness of diagram (F), experiments will be carried out on the infra-red spectra of the compounds in question in solution.

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REFERENCES

[1] T. Urbański, *On hydrogen bonds in some nitroalcohols (on the basis of infra-red absorption spectra)*, Bull. Acad. Polon. Sci. Cl. III **4** (1956), 87.

[2] T. Urbański, *On the structure of some aliphatic nitrocompounds*, Bull. Acad. Polon. Sci. Cl. III **1** (1953), 239.