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# Intramolecular Interaction between Hydroxyl Group and π-Electrons. XXIV.[1] The Interaction Involving the Cyano Group

Michinori Ōki and Takashi Yoshida

*Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo*

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The infrared O–H stretching spectra of various 1- and 2-cyano alcohols have been measured, and the presence of intramolecular O–H···π interaction has been detected. Some discussion of the confirmation of such alcohols is given.

Various olefins and aromatics are known to behave as proton acceptors to establish interaction between the hydroxyl group and π-electrons. Since we have reported in a previous paper[1] that the π-electrons of the carbonyl group, which involves the hetero atom, can act as proton acceptors, we have now naturally extended the work to the π-electrons of the carbon-nitrogen system. Although the intramolecular interaction between the hydroxyl group and π-electrons of the cyano group was briefly treated by Allerhand and Schleyer,[2] and although the possibility of such an interaction was implied by Casadevall *et al.*,[3] more precise work has been clearly needed. The purpose of this paper is to present the results of our investigation.

## Experimental

*Materials.* All the cyano alcohols used in this study were known compounds and were prepared according to the published methods. The purity of the sample was checked prior to use.

*Infrared Spectra.* The spectra were recorded on a Perkin Elmer 112 G grating spectrophotometer. The samples were dissolved in carbon tetrachloride to make up a 3—6 mmol/*l* concentration. The absorption bands due to the hydroxyl group of the 1-cyano alcohols were either completely symmetric or slightly unsymmetric. Thus, no effort was made to divide these bands into their components. On the other hand, 2-cyano alcohols showed two-peaked bands which were divided into symmetric curves, as has been described previously.[4]

## Results and Discussion

*1-Cyano Alcohols.* The O–H stretching ($\nu_{O-H}$) absorptions of 1-cyanocyclohexanol are given in Fig. 1.

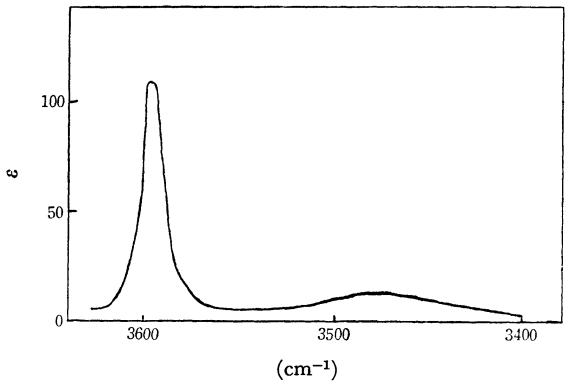



Fig. 1. The $\nu_{O-H}$ absorption of 1-cyanocyclohexanol.

1) M. Ōki, H. Iwamura, J. Aihara, and H. Iida, This Bulletin, **41**, 176 (1968).

2) A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 866 (1963).

3) E. Casadevall, M. Lasperas, and L. Mion, *Tetrahedron Lett.*, **1970**, 1525.

4) M. Ōki, H. Iwamura, T. Murayama, and I. Oka, This Bulletin, **42**, 1986 (1969).

It will be seen that 1-cyanocyclohexanol shows a broad and weak absorption at *ca.* 3480 $cm^{-1}$ and a sharp and strong absorption at *ca.* 3600 $cm^{-1}$. This feature is generally observed with 1-cyano alcohols. Since the intramolecular O-H···N distance is too far to form a hydrogen bond, the absorption at the lower frequency may be attributed to the presence of the intermolecular hydrogen bond. Indeed, when the concentration of 1-cyano alcohol is increased, the absorption at the lower wave number increases in its intensity. The presence of the intermolecular hydrogen bond at the concentration where other ordinary alcohols exist solely as monomers may be attributed to the larger proton-donating ability of the hydroxyl group as a result of the electronic effect of the cyano group. In the following discussion, it is assumed that the effect of the absorption band resulting from the intermolecular hydrogen bond on the monomeric absorption is negligible, and so only the data on the monomeric band are given.

Table 1. The $\nu_{O-H}$ data of 1-cyano alcohols derived from ketones [RR'C(OH)CN]

| R | R' | $\nu_{OH}$ ($cm^{-1}$) |
|---|---|---|
| $CH_3$ | $CH_3$ | 3601 |
| $CH_3$ | $C_2H_5$ | 3602 |
| $CH_3$ | $CH_3(CH_2)_2$ | 3602 |
| $CH_3$ | $(CH_3)_2CH$ | 3605 |
| $(CH_2)_5$ | | 3594 |

The data concerning the $\nu_{O-H}$ absorption of 1-cyano alcohols derived from ketones are given in Table 1. It will be seen that 1-cyano alcohols prepared from ketones show only one symmetric absorption, the location of which is fairly low when compared with the cases of normal tertiary alcohols (*ca.* 3616 $cm^{-1}$). The results can be interpreted in either of the following two ways: 1) All the hydroxyl groups are free; in other words, the hydroxyl group does not interact with the cyano group. The shift of the band to the lower frequency is caused by the high electronegativity of the cyano group.[5] 2) All the hydroxyl group interacts with the cyano groups, and the lower shift of the $\nu_{O-H}$ is to be ascribed to the interaction.

A comparison of the data with those of the corresponding ethynyl compounds may throw light on this problem.

Since propargyl alcohol is known from microwave spectroscopy[6] to exist solely as a conformation in which the hydroxyl group is close to the $\pi$-electrons, it is natural to assume that propargyl alcohol takes a similar conformation in solution with a nonpolar solvent. Indeed, propargyl alcohol has been reported to show only one $\nu_{O-H}$ band, at 3620 $cm^{-1}$, in a carbon tetrachloride solution[7]; its conformation has been suggested to be as such that the hydroxyl group and $\pi$-electrons interact because of the lower location of the band.

1-Ethynylcyclohexanol shows only one symmetric $\nu_{O-H}$ band, at 3607 $cm^{-1}$. Although this location could be ascribed to the ordinary tertiary alcohol, because 1-adamantanol and 1-hydroxybicyclo [2.2.2]-octane are known to give bands at 3605 and 3608 $cm^{-1}$ respectively,[8] it is also known that other non-rigid tertiary alcohols never give the $\nu_{O-H}$ band below 3610 $cm^{-1}$.[9] Therefore we choose to attribute the lower location of the $\nu_{O-H}$ band of 1-ethynylcyclohexanol to the presence of the O-H···$\pi$ interaction. Then, the rather large shift of the $\nu_{O-H}$ absorption of 1-cyanocyclohexanol to 3594 $cm^{-1}$ is in the direction to be expected from the electronegativity.

Table 2. The $\nu_{O-H}$ data of 1-cyano alcohols derived from aldehydes [RCH(OH)CN]

| R | $\nu_{OH}$($cm^{-1}$) | $\beta/\alpha$ |
|---|---|---|
| $CH_3$ | 3607 | 1.0 |
| $C_2H_5$ | 3611 | 1.44 |
| $CH_3(CH_2)_2$ | 3609 | 1.87 |
| $(CH_3)_2CH$ | 3614 | 1.48 |
| $(CH_3)_3C$ | 3612 | 2.0 |

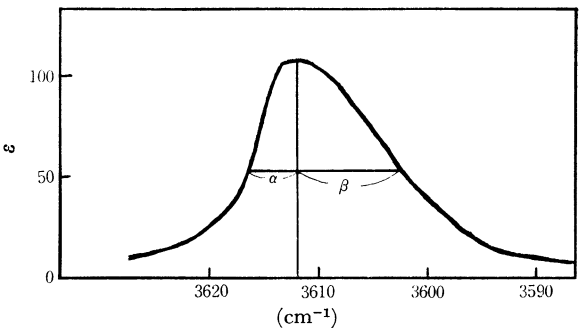



Fig. 2. The $\nu_{O-H}$ absorption of $\alpha$-cyanoneopentyl alcohol, showing the notation of $\alpha$ and $\beta$.

Considering these factors, it is most probable to assume that the 1-cyano alcohols shown in Table 1 give only one $\nu_{O-H}$ absorption because of the sole presence of a conformer in which the hydroxyl group and $\pi$-electrons of the cyano group interact with each other.

On the other hand, 1-cyano alcohols derived from aldehydes show unsymmetric $\nu_{O-H}$ bands, as is shown in Table 2. The $\alpha$ and $\beta$ in Table 2 are the values proposed by Rader and Aaron[10], as is shown in Fig. 2. That is, the line corresponding to the half-band-width is cross-cut by a straight line corresponding to the maximum absorption. The $\alpha$ value is, then, the section of the higher-frequency side, and $\beta$, that of the lower-frequency side. If the $\beta/\alpha$ value is larger than unity, it can be interpreted as that there is a small peak on the lower-frequency side. As may be seen in Table

5) In phenol derivatives, if a compound carries an electron-withdrawing substituent at the *m*- or *p*-position, the $\nu_{O-H}$ band appears at the lower frequency. See, for example, P. J. Stone and H. W. Thompson, *Spectrochim. Acta*, **10**, 16 (1957).

6) E. Hirota, *J. Mol. Sepctry.*, **26**, 335 (1968); K. Bolton, N. L. Owen, and J. Sheridan, *Nature*, **217**, 164 (1968).

7) P. von R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Amer. Chem. Soc.*, **80**, 6691 (1958).

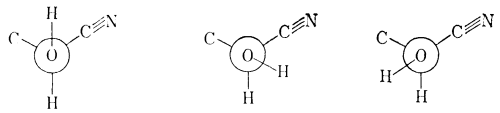
8) L. Joris, P. von R. Schleyer, and E. Ōsawa, *Tetrahedron*, **24**, 4759 (1968).

9) M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

10) H. S. Aaron and C. P. Rader, *J. Amer. Chem. Soc.*, **85**, 3046 (1963); H. S. Aaron, C. P. Ferguson, and C. P. Rader, *ibid.*, **89**, 1431 (1967).

2, all the cyano alcohols derived from aldehydes except acetaldehyde give $\nu_{O-H}$ absorptions which possess $\beta/\alpha$ values larger than 1.

These results can also be interpreted in two ways. The two bands could arise from the free and the interacting forms of the cyano alcohols, or, the reason could be the presence of the two interacting conformations. Either way is possible, but the present authors wish tentatively to ascribe the phenomena to the second reason in consideration of the results with ketone-cyanohydrin and propargyl alcohol.



(1) (2) (3)

Three conformations, **1**, **2**, and **3**, are possible for the aldehyde-cyanohydrins concerning the rotation about the C–O axes. Since it has been assumed that all the molecules are intramolecularly O–H···$\pi$ interacting species, the conformation **3** may be neglected in the following discussion. The hydroxyl proton and the cyano group are too far separated to interact with each other, and the geometry is not favorable for the interaction. There are, then, clearly two conformations in which O–H and $\pi$-systems can interact, and these conformations may be reflected in the $\nu_{O-H}$ absorptions.

Next, the question may be raised as to which conformation corresponds to the absorption at a higher frequency. There is no definite answer to this question. However, from the analogous consideration in secondary alcohols[9], the O–H absorption at the higher frequency may be assigned to the conformation **2**, since the conformation **4** of secondary alcohols is known to give rise to absorptions at higher freqencies than does the conformation **5**.

(4) (5)

To a question why aldehyde-cyanohydrins having the bulkier alkyl group give large $\beta/\alpha$ values, we wish to attribute this tentatively to the shift to the lower freqencies of absorption corresponding to the conformation **1** because of the stronger interaction caused by the proximity of the two groups due to the buttressing effect of the alkyl group. A similar effect was also observed with cyano alcohols derived from alkyl methyl ketones, where alkyl is a bulky group.

Table 3. The data of 2-cyano alcohols $RR'C(OH)CH_2CN$

| R | R′ | $\nu_h$[a] | $\nu_l$[a] | intensity ratio[b] |
|---|---|---|---|---|
| H | H | 3634 | 3615 | 0.99 |
| H | $CH_3$ | 3625 | 3607 | 1.83 |
| $CH_3$ | $CH_3$ | 3611 | 3593 | 0.69 |

a) The suffixes *h* and *l* refer to absorptions at higher and lower frequencies, respectively.

b) The intensity ratios were obtained by taking the ratio of the products of molecular extinction coefficients and the half-band widths after graphical separation, corresponding to the $A_l/A_h$ value.

That is, a slightly unsymmetrical $\nu_{O-H}$ band is observed for those compounds, although it is hard to estimate the difference from unity in the $\beta/\alpha$ value because of the low degree of unsymmetrv.

*2-Cyano Alcohols.* The $\nu_{O-H}$ data of several 2-cyano alcohols are given in Table 3. Apparently these alcohols give two $\nu_{O-H}$ absorptions, the two maxima being separated by *ca.* 18 $cm^{-1}$. Although the shifts are observed with the bands at higher frequencies, they are located at the ordinary positions for the free hydroxyls when the class of the alcohols is considered. Therefore, those at the higher wave numbers are assigned to the free hydroxyl group.

The separation of the two bands at the higher and the lower frequencies, namely, *ca.* 18 $cm^{-1}$, is a little too large to attribute its origin to the presence of the second conformer of the alcohol. The intensity ratios are also too small to attribute to the conformational heterogeneity of the alcohols.[8,9,11] These facts together with a consideration of the molecular models, which reveals that the hydroxyl group can come close to the $\pi$-electron system, lead to the conclusion that the band at the lower wave number should be assigned to the O–H···$\pi$ interacting species, although it could include absorption due to the free hydroxyl group of the second conformer in the cases of primary and secondary alcohols.

The higher intensity ratios for propylene cyanohydrin may be attributed to the steric effect between the cyano and the methyl groups, through which the conformation with the hydroxyl group and the cyano group in the gauche relation is relatively favored. However, no explanation of the results with isobutylene cyanohydrin is possible using this idea. Clearly, further study is needed to understand these numerical values.

11) The separation of the two peaks and the intensity ratio ($A_l/A_h$) due to the conformational heterogeneity of secondary alcohols are usually 10—14 $cm^{-1}$ and 3—5 respectively.[8,9]