Intramolecular Hydrogen Bonds. III.[1] Cyanoalkanols

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The intramolecular hydrogen bonding in some cyanoalkanols in dilute carbon tetrachloride solutions was previously investigated by means of infrared measurements in the OH-stretching region near 3 μ.[2,3] Acetaldehyde- and cyclohexanone-cyanohydrins show only one absorption band, at 3604 and 3594 cm^{-1} respectively, the latters are lower by ca. 20 cm^{-1} than those of the corresponding unsubstituted secondary and tertiary alcohols. Flett[2] suggested that the lowering in frequency is to be attributed to the electron-attracting effect of the cyano group and that the OH bands are, then, due to the free OH group. On the other hand, Allerhand and Schleyer[3] attributed the lowering in frequency to the formation of an internal

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[1] Part II: N. Mori, S. Ōmura and Y. Tsuzuki, This Bulletin, 38, 1037 (1965).

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[2] M. St. C. Flett, *Spectrochimica Acta*, 10, 21 (1957).

[3] A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, 85, 866 (1963).

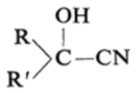
hydrogen bond of the OH group with the π-electrons of the cyano group; they based their suggestion on a comparison with the OH frequency (3620 cm^{-1}) of propargyl alcohol, which had been assigned to the OH group internally banded to the π-electrons of the triple bond.4) However, the re-investigation of propargyl alcohol, which has recently been reported,5) shows the frequency to be that of the free OH group. Thus, the basis for the assignment given for the cyanoalkanols by Allerhand and Schleyer has been lost. Accordingly, we must re-investigate to determine whether or not such α-cyanoalkanols form intramolecular hydrogen bonding. This problem has now been solved through the infrared measurements of a series of α-cyanoalkanols. Further, this paper will report on the limitation of intramolecular hydrogen bonding* through the length of an alkylene chain in the series of ω-cyanoalkanols, NC(CH$_2$)$_n$OH.

Experimental

α-Cyanoalkanols were prepared from the corresponding aldehydes and ketones in the usual manner, while 4- and 10-cyanoalkanols were synthesized from the corresponding haloalkanols by reaction with potassium cyanide6); b. p. 130°C/14 mmHg (n_D^{25} = 1.4371) and 178—179°C/8 mmHg. β-Cyanoethanol was commercially obtained and was fractionally distilled; b. p. 110°C/15 mmHg.

Infrared measurements in the OH-stretching region were carried out at 25°C with solutions of 0.004 mol./l. in carbon tetrachloride on a Perkin Elmer 21 spectrophotometer equipped with a lithium fluoride prism. The cell used was 3 cm. long, and the slit width was always 0.029 mm. The observed frequencies were calibrated on the standard of atmospheric vapor and within a range of error of ±1 cm^{-1}. At that concentration, there was observed, in addition to a strong absorption band near 3600 cm^{-1}, a very weak and broad bond at 3470—3490 cm^{-1} which varied with the concentration; the latter is indicative of some intermolecular hydrogen bonding. The infrared data are summarized in Table I.

TABLE I. SUMMARY OF INFRARED DATA



Compound	R	R′	ν_{OH}(cm^{-1})*	log I_0/I	$\Delta\nu_{1/2}$
I	H	H	(3623) 3610	0.16 0.86	16 28
II	H	Me	(3615) 3604a)	0.10 1.00	12 27
III	Me	Me	(3608) 3599	0.10 1.02	8 22
IV	Me	Et	(3606) 3599	0.15 0.97	8 24
V	-(CH$_2$)$_5$-		3591b)	1.08	23
			NC-(CH$_2$)$_n$-OH		
	n				
VI	2		(3631)c) (3610)c)	0.57 0.46	28 28
VII	3		36403)		
VIII	4		3638d) (3622)	0.68 0.19	20 18
IX	10		3637 (3621)	0.70 0.20	24 10

a) reported 36042) or 36073); b) reported 35942); c) reported 3625 and 36102) or 3632 and 36173), respectively; d) reported 3639.3)

* Parentheses show separated-band frequencies, the errors for which are in a range of ±2 cm^{-1}.

Results and Discussion

The spectrum of cyclohexanone cyanohydrin (V) includes only one symmetric sharp band, at 3591 cm^{-1}, while the other α-cyanoalkanols (I—IV) each show a band rather broadened on the higher frequency side. 4- and 10-cyanoalkanols (VIII and IX) each show a band somewhat broadened on the lower frequency side. The lack of symmetry of the bands may be produced by the overlap of symmetric bands of the Lorentz type, which should be assigned to the OH groups in the conformational isomers possible by rotation around the C$_\alpha$-O bond, as will be presented below. The symmetric bands can graphically be separated from the original unsymmetric band, e.g., as is shown in Fig. 1. β-Cyanoethanol (VI) apparently

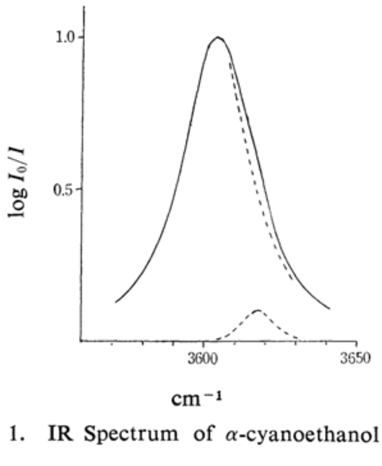


Fig. 1. IR Spectrum of α-cyanoethanol (II).

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4) P. von R. Schleyer, D. S. Trifan and R. Bacskai, ibid., **80**, 6691 (1958).

5) B. Jordanov, A. Jovtscheff, S. Spassov, B. Blagoev and M. Agova, *Tetrahedron*, **20**, 903 (1964).

* The term "Hydrogen bonding" will herein be replaced by the term "Interaction," which has been proposed for hydrogen bonding between an OH group and π-electrons by M. Ōki and H. Iwamura, This Bulletin, **32**, 567 (1959).

6) P. Chuit and J. Hausser, *Helv. Chim. Acta*, **12**, 463 (1929).

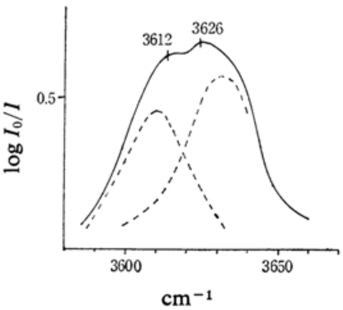


Fig. 2. IR Spectrum of β-cyanoethanol (VI).

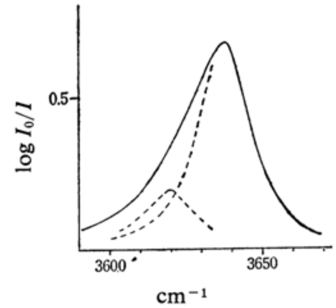
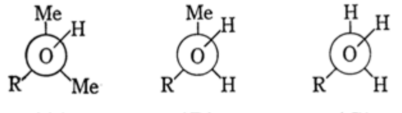


Fig. 3. IR Spectrum of 4-cyanobutanol (VIII).

shows partially-resolved doublet, with maxima at 3626 and 3612 cm^{-1}, whose frequencies agree with those previously reported by Flett,²⁾ but this doublet can not be separated into two symmetric bands which have maxima at the above frequencies and which by overlapping with each other can reproduce the doublet. However, it can be synthesized from the two symmetric bands whose maxima are at 3631 and 3610 cm^{-1}, as Fig. 2 shows. This separation seems to be rather reasonable as will be discussed below. The frequencies of the separated bands are summarized in Table I, but they are somewhat rough because of the graphical separation and the relatively poor resolv ing power of the spectrophotometer employed.

According to the infrared study by Ōki and Iwamura⁷⁾ of the rotational isomerism around the C-O bond in alcohols, a methyl group skew to the OH group has a steric effect serving to make the OH frequency lower by ca. 13 cm^{-1}, as is shown in Table II.

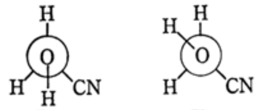
TABLE II. THE ROTATIONAL ISOMERS OF ALCOHOLS AND THEIR OH FREQUENCIES



	(A)	(B)	(C)
ν_{OH} cm^{-1}	3617	3627	3640

R: H or alkyl.

In consideration of the above assignments, the lower and the higher frequency band of cyanomethanol (I) should be assigned to the OH groups of Ia and Ib respectively.

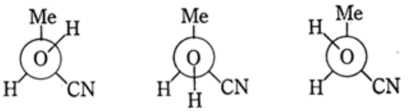


Ia Ib

3610 cm^{-1} 3623 cm^{-1} $\Delta\nu$: 13 cm^{-1}

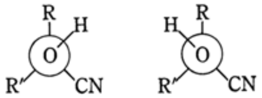
The shift of the higher frequency band by 17 cm^{-1} from that of the corresponding rotational isomer (C) of ethanol, may be attributed to the electron-attracting effect of the cyano group; this is also true with the other α-cyanoalkanols, but the shifts is drastically decreased by the intervention of a methylene group, as may be seen in β-cyanoethanol (VI), whose free OH frequency is 3631 cm^{-1}. Although the separation between the two bands, $\Delta\nu$, is only 13 cm^{-1}, equal to that in the case of ethanol, the OH grop in Ia interacts with the π-electrons of the cyano group, because its absorption intensity is very high with respect to that of the OH in Ib.

Similarly, the follwing assignment may be given for the other α-cyanoalkanols (II—V):



IIa IIb IIc

For II 3604 cm^{-1} ca. 3615 cm^{-1}
$\Delta\nu$: 11 cm^{-1}



(a) (b)

For III and IV 3599 cm^{-1} ca. 3607 cm^{-1} $\Delta\nu$: 8 cm^{-1}
For V 3591 —

The difference in frequency between Ib and IIc, 8 cm^{-1}, may result from the steric effect of the methyl group.

In the case of compound II, the 3604 cm^{-1} of the symmetric, interacted OH band lies just between the OH frequencies of forms Ia and IIIa. This compound can take two interacted forms, IIa and IIb, which correspond to forms IIIa and Ia respectively. Accordingly, one may say that the OH frequencies of forms IIa and IIb are close to 3604 cm^{-1}, that the major component of the band is due to the OH group

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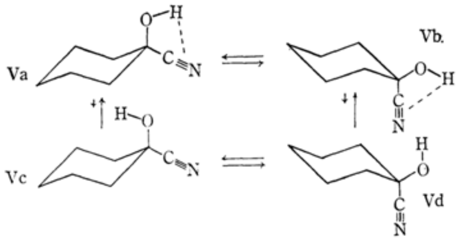
7) M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959). The same assignments were also reported by F. Dalton, G. D. Meakins, J. H. Robinson and W. Zaharia, *J. Chem. Soc.*, **1962**, 1566.

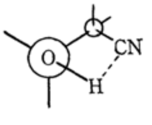
in form IIb, and that its minor component is due to the OH in form IIa, since form IIb should be thermodynamically more stable than form IIa.

The OH band of cyclohexanone cyanohydrin (V) is symmetric, as has been mentioned above; this indicates that all the molecules substantially exist in at least one of the interacted forms, Va or Vb:

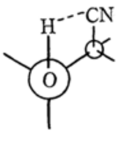


Form Vc may be negligible because the axial hydrogens on C_3 and C_5 sterically repel the hydroxyl-hydrogen atom, thus directing it towards the cyano group, and form Vd is less stable than Vb because, similarly, the latter is possibly more stabilized through the interaction between the OH group and the π-electrons of the cyano group. Let us now consider which of the forms, Va or Vb, is more stable. The difference in free energy between the equatorial and the axial OH group is 0.4—0.9 kcal./mol.,[8] which is higher than the value of 0.15—0.25 kcal./mol. for the cyano group.[9] The difference between the respective, averaged values, 0.45 kcal./mol., corresponds to a K value of 2.1 in the van't Hoff isotherm: $\Delta G^\circ = -\boldsymbol{R}T \ln K$. This means that the number of molecules taking form Vb is larger by a factor of roughly 2.1 than that taking form Va. Further, the symmetric shape of the band can be confirmed from this population of molecules and by the fact that the difference in frequency between axial and equatorial tertiary OH groups is generally 6 cm^{-1} at most.[10] That the frequency of this compound is lower by 8 cm^{-1} than those of compound III and IV may be explained in terms of the *gem*-dialkyl effect,[11] by which the O-C_α-CN bond angle is decreased, thus bringing the OH and the cyano group closer together.

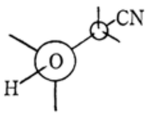
For β-cyanoethanol (VI), one may consider nine rotational isomers to be possible by rotation around the single bonds: three (the number of rotational isomers around the C_α-O bond) times three (the number of rotational isomers around the C_α-C_β bond). Eight of these form four pairs of mirror images, and only one pair of VIa and VIb are those favorable for intramolecular interaction. Since forms VIa and VIb contain, in addition to the methyl effect, interaction between the OH and the β-cyano group, the interacted OH frequency will be lower than the 3627 cm^{-1} of the above-mentioned ethanol B. On the other hand, form VIc may be the least strained conformation of those free from interaction. Thus the OH frequency will be near the 3640 cm^{-1} of ethanol C. The observed frequencies of 3610 and 3631 cm^{-1} are in accordance with those expected and are rather more reasonable values than those of the apparent peaks (3612 and 6326 cm^{-1}). The interacted OH frequency of 3617 cm^{-1} reported by Allerhand and Schleyer might be incorrect because the frequency was that of the shoulder of band.



VIa



VIb



VIc

Compounds VIII and IX are free from intramolecular interaction. The bands at 3622 and 3637 cm^{-1} may be due to the free OH groups in the rotational isomers formed by rotation around the C_α-O bond, such as forms B and C of ethanol respectively. The absence of interaction may be due to the formation of a larger ring through interaction being thermodynamically more difficult.

From the above findings, it may be concluded that the OH group in the α-cyanoalkanols interacts with the π-electrons of the cyano group, and that the interaction in the series of $NC(CH_2)_n$-OH occur when n is 1 or 2, as has previously been reported[3].

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[8] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Company, New York, N. Y. (1962), p. 236.

[9] N. L. Allinger and W. Szkryblo, *J. Org. Chem.*, **27**, 4601 (1962); B. Rickborn and F. R. Jensen, ibid., **27**, 4606 (1962).

[10] A. R. H. Cole, G. T. A. Müller, D. W. Thornton and R. L. S. Willix, *J. Chem. Soc.*, **1959**, 1218.

[11] P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 1368 (1961), and the references cited therein.