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THE STRUCTURE OF ω-CYANOALKANOLS (I)

INFRARED SPECTROMETRIC STUDIES

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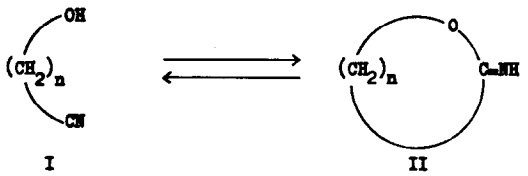
ω-Cyanoalkanols have long been supposed to be simple chain molecules. We have considered that the molecules containing a electrophilic hydrogen of hydroxyl group and a cyano group with high electron density can cause the covalent addition. The purpose of our present investigation is to study the infrared spectra of ω-cyanoalkanol (I) in order to elucidate the presence of cyclic isomer, that is, imino-lactone (II) at ordinary temperature.



I II

As shown in Table 1 and Fig. 1, all of these compounds exihibit the characteristic peaks in the region of 1640 - 1780 cm^{-1}. These absorption bands might be assigned as a stretching vibration of C=N bond. It is well known that the bathochromic shift is usually observed when the ring strain in the cyclic compounds such as lactone, lactam, ketone, and others is reduced. [1)]

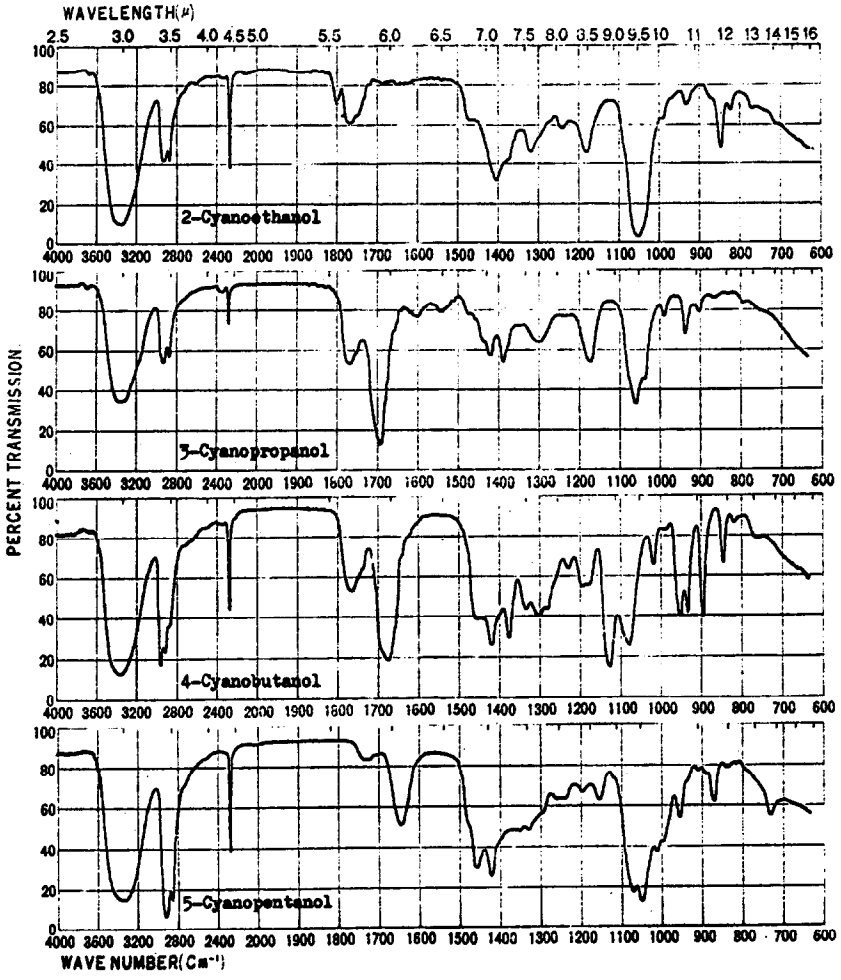


FIG. 1

Infrared Spectra of ω-Cyanoalkanols

TABLE 1

The Absorption Frequencies of C≡N Bond

n	Compounds	Ring member	ν C≡N (cm^{-1})
2	2-Cyanoethanol	4	1772
3	3-Cyanopropanol	5	1695
4	4-Cyanobutanol	6	1676
5	5-Cyanopentanol	7	1643

Our data accord with this fact and suggest that imino group is exocyclic, because the behaviour of imino absorptions is especially similar to that of exocyclic lactone carbonyl group. On assuming the equillibrium between I and II, 3-cyanopropanol and 4-cyanobutanol which can form stable five and six membered ring respectively, might be more favorably in cyclic forms than 2-cyanoethanol and 5-cyanopentanol.

Our data in Fig. 1 show that the intensities of C≡N absorption of 3-cyanopropanol and 4-cyanobutanol are much stronger than 2-cyanoethanol and 5-cyanopentanol.

It seems reasonable to conclude that there exists the tautomerism between ω-cyanoalkanols and their corresponding imino-lactones at ordinary temperature. Studies are still in progress to provide further evidence of this point.

Preparation of ω-cyanoalkanols

2-Cyanoethanol was commercially obtained and fractionally distilled; b.p. 122°C/23 mmHg (Anal. % Found; C, 50.7; H, 7.3; N, 19.6).

3-Cyanopropanol was prepared from 3-chloropropanol in the usual manner[2] by the reaction with potassium cyanide; b.p. 110°C/ 21 mmHg.

4-Cyanobutanol and 5-cyanopentanol were prepared by reacting the correspond-

ing lactone and anhydrous ammonia in the presence of powdered alumina.

4-cyanobutanol; b.p. 75°C/2 mmHg 'Anal. % Found; C, 60.4; H, 9.0; N, 13.9)

5-cyanopentanol; b.p. 107°C/2.5 mmHg (Anal. % Found; C, 63.5; H, 10.2; N, 12.3)

Infrared measurements

Infrared measurements were carried out at 25°C with liquid film on a Nihon Bunko Model DS-201 spectrometer equipped with a NaCl prism.

The observed frequencies were calibrated by the standard polystyrene film.

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2. Yu.K.Yur'ev, G.P.Mikhaĭlovskiĭ and S.Z.Shapiro, Zhur. Obshchoĭ Khim., 19, 2217 (1949); through Chem. Abs., 44, 4460 (1950).