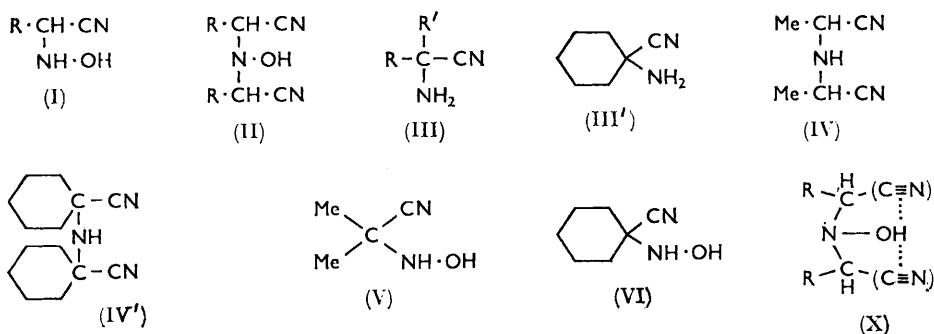


751. *NN*-Di-(1-cyanoalkyl)hydroxylamines. Part II.¹ Infrared Spectra.

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The infrared spectra of *NN*-di-(1-cyanoalkyl)hydroxylamines (II) and related compounds were studied. Intramolecular interaction between the OH and the CN groups is rather weak, but a larger effect is noticed between the one OH and the two CN groups. From the results, the configuration of the compound is deduced. For $\delta(N-H)$, an extraordinary low-frequency but distinct band is observed with α -hydroxyamino-nitrile (I). Several other characteristic bands are assigned, and the effect of an α -nitrogen atom to the $\nu(C\equiv N)$ is examined. The unshared electrons on the hydroxyamino-nitrogen of (II) are seen in the $\nu(C\equiv N)$ frequency not to behave as in normal amines.

THE infrared spectra of hydroxylamine and its simple derivatives have been studied by several authors.²⁻⁵ Comparison of their results and those for the related compounds, obtained by a deuteration technique, we tried to assign the frequencies of the infrared spectra of α -hydroxyamino-nitriles (I) and *NN*-di-(1-cyanoalkyl)hydroxylamines (II).



Our particular aim was to find the characteristic bands of compounds (I) and (II) for their easier differentiation, but several interesting features were found in the spectra. The main bands and their assignments are tabulated in Tables 1 and 2.

O-H and N-H Stretching Frequencies.—Solid nitriles (I) have two bands at 3175 ± 30 and 3273 ± 27 cm^{-1} in these regions; the lower-frequency band is likely to shift to lower frequency with increasing size of R. α -Hydroxyaminoisobutyronitrile (V) and α -hydroxyaminocyclohexanonitrile (VI), having no α -hydrogen atom, show only one, very strong band at higher frequency.

In carbon tetrachloride solution, the nitrile (I) shows intense O-H and N-H absorption bands of the monomer at 3605 ± 2 and 3298 ± 2 cm^{-1} , respectively. The dinitrile (II) has bonded O-H stretching frequency at 3331 ± 3 cm^{-1} in the solid, and a monomer O-H absorption at 3583 ± 13 cm^{-1} in carbon tetrachloride. The size of group R does not cause such changes of frequency as in (I).

When one R group of (II) is methyl, as in *NN*-di-(1-cyanoethyl)- and *N*-(1-cyanodecyl)-*N*-(1-cyanoethyl)-hydroxylamines, the O-H band is split in the solid. In carbon tetrachloride solution ($<10^{-3}M$) *NN*-di-(1-cyanoethyl)hydroxylamine shows only one absorption band, but the other shows two, at 3440 and 3570 cm^{-1} . As the intensity of the 3440 cm^{-1} band decreases with increasing dilution (Fig. 1), this is assigned to the dimer O-H stretching

¹ Part I, *J.*, 1961, 4063.

² Giguere and Lui, *Canad. J. Chem.*, 1952, **30**, 948.

³ Nightingale and Wagner, *J. Chem. Phys.*, 1954, **22**, 203.

⁴ Munoz, Mathis, and Mathis-Noël, *Compt. rend.*, 1957, **244**, 1751.

⁵ Davies and Spiers, *J.*, 1959, 3971.

TABLE I.
 Frequencies (cm.⁻¹) of α -hydroxyaminonitriles (I) in mulls.*

Assign. \ R	H	Me	Et	Pr ^a	Hexyl	Nonyl	Pr ⁱ	Cyclohexyl	NHMe·OH ^b
$\nu(\text{O-H})^c$			3607	3604	3606				$\begin{cases} 3656^c \text{ m} \\ 3644^c \text{ m} \\ 3627^c \text{ m} \end{cases}$
$\nu(\text{N-H})^c$			3300	3297	3298				
$\nu(\text{O-H})$	3185s	3215vs	3185s	3160s	3155s	3155s	3300vs	3290vs	3550—3000vs
or									
$\nu(\text{N-H})$	3289s	3277vs	3247s	3261s	3254s	3268s			3269s
$\nu(\text{C}\equiv\text{N})$	2240w	2239w	2225w	2227w	2227w	2232w	2232w	2232w	
$\delta(\text{N-H})$	1500m	1506m	1503m	1497m	1497m	1497m	1495m	1486m	
$\delta(\text{O-H})$	1420m	1436m	(~1450) ^d	(~1450) ^d			1418m	1418m	1405m
	1320m	1323m	1346w	1328w	1326w	1340m	1233m	1355w	
	1260m	1290m	1334w	1261w	1307w	1326m	1212s	1335w	
	1160s	1197w	1284w	1223w	1285w	1309w	1186m	1279m	
		1185w	1244w	1164w	1247w	1297m	1160w	1227m	
		{1103s	1172m	1120m	1205w	1285w		1165m	
		{1090sh	1112m	1101w	1163w	1255w		1123m	
			1035w	1062w	1120w	1228m		1069w	
					1093w	1210w			
					1059m	1190w			
					1043m	1165w			
					1000m	1127w			
						1098s			
						1077m			
						1062m			
						1052m			
						1030s			
$\nu(\text{N-O})$	{ 977s	960m	951m	935w			1059s	{ 1040sh	1034vs
	{ 1024s	1014m	{ 1017sh	{ 1012m			1019s	{ 1030s	994m
	{ 898m	882m	{ 1009m	{ 1002sh			971s	{ 967s	
			907m	898w			947w	{ 946m	
								907s	
	856m	805w	849w	884w				894s	
	787m		774w	867w	935w	1020m	914s	847m	
	741m		748w	810w	916w	990m	866s	821w	
				739w	892w	964w	780m	789w	
					840w	950m		725m	
					780w	936m			
					768w	890w			
						872m			
						848m			
						800w			
						790m			

* Nujol and hexachlorobutadiene were used except those shown as soln.

^a Solution in carbon tetrachloride; <10⁻³ mole/l. ^b Liquid film; data taken from ref. 5. ^c Vapour. ^d Overlapped with C-H modes.

frequency. The absence of the dimer O-H band from the spectrum of NN-di-(1-cyanoethyl)hydroxylamine is possibly only a solvent effect. A dimeric form of (II) is thus possible, where one R group at least is methyl. Probably the small steric effect of a methyl group makes possible a dimeric form arranged like the simple cyclic structure of an oxime.⁶ The two split O-H bands are affected by deuteration. Since the bands at the higher frequencies, 3450 and 3436 cm.⁻¹, for both compounds as solids, are very close to the dimer frequency, 3440 cm.⁻¹, found in the carbon tetrachloride solution, it may be assumed that the two compounds can be either the dimeric or polymeric in the solid.

The monomer O-H stretching frequencies of (I) and (II) are somewhat lower than those of methylhydroxylamines,⁵ ascribable to the effect of the CN group(s). This interaction is not as strong as the intermolecular hydrogen bonding between OH and CN groups,^{7,8}

⁶ Bellamy and Hallam, *Trans. Faraday Soc.*, 1959, **55**, 220.

⁷ Schleyer and Allerhand, *J. Amer. Chem. Soc.*, 1962, **84**, 1322.

⁸ Ferstandig, *J. Amer. Chem. Soc.*, 1962, **84**, 1323.

TABLE 2.

		Frequencies (cm. ⁻¹) of <i>NN</i> -di-(1-cyanoalkyl)hydroxylamines.*					
Assign.	R ¹ R ²	Me	Et	Pr ⁿ	Hexyl	Me	Me ₂ N·OH ^b
		Me	Et	Pr ⁿ	Hexyl	Nonyl	
ν(O-H)	}	3581 ^a	3595 ^a	3594 ^a		3570 ^a	3651—3621 ^c ms
		3450vs				3440 ^a	
2 × δ(O-H)	}	3330vs	3334s	3328s	3333s	3436s	
		2750w	2770w	2770w		3333s	
ν(C≡N)		2245w	2245w	2247w	2242w	2242w	
δ(O-H)	}	1409s	1391s	1390m		1395m	1313vw
		1377w				1303w	1204m
		1340m					1170
		1315m	1307m	1310w	1310m	1113w	1161sh
		1286m	1242w	1274w	1229w	1117m	1090
		1149m	1138w	1189w	1134w	1063m	1054w
		1133m	1100w	1127w	1121w		
		1105m	1065m	1116w			
		1090m	1014w				
		1062s	1065m	1071m	1080m		
ν _{as} (C-N-C)	}		1043w	1043w	1063w	1052m	999m
			1014w	1017m	1026w	1005w	
					986w	956m	
					963w	915w	
					936w	900w	
					890w	845m	
						826m	
ν(N-O)		952s	942m	925m	911w		956ms
ν _{sym} (C-N-C)	}	829s	833sh	829m	846m		807s
			823m	816m	821m		
		758m	765w	743	782w	789m	
			675w	720w	723m	723m	
		675	676w	675			

* See footnotes to Table 1.

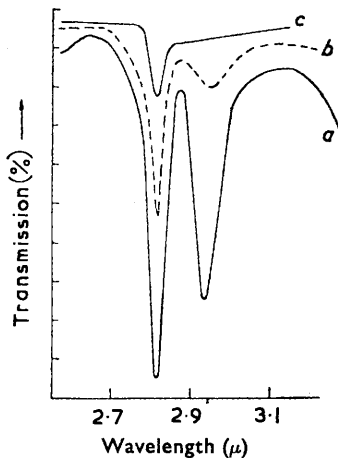


FIG. 1. Effect of concentration on the $\nu(\text{O-H})$ band of *N*-(1-cyanoethyl)-*N*-(1-cyanoethyl)hydroxylamine (in CCl_4).

(a) Saturated solution ($< 10^{-3}\text{M}$); (b) $a/4$;
(c) $a/16$.

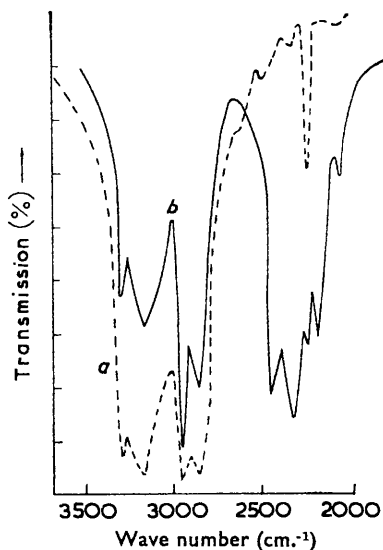


FIG. 2. Infrared spectrum of α -hydroxyaminovaleronitrile(hexachlorobutadiene mull).

(a) Normal sample; (b) deuterated sample.

and the O-H...N intramolecular hydrogen bond,⁶ but it cannot be neglected. The greater effect can be seen in (II) with two CN groups. It appears that NN-di-(1-cyanoalkyl)hydroxylamines exist in dilute solution predominantly as configuration (X), *i.e.*, the three functional groups are close to one another.

Deuteration of the amino-nitrile (I) decreases the intensity of the bands in the $\nu(\text{C-H})$ region (2500—2990 cm^{-1}) though the decrease is not so great as for $\nu(\text{O-H})$ and $\nu(\text{N-H})$, and produces a series of bands at 2050—2200 cm^{-1} . It is clear that the strong $\nu(\text{C-H})$ bands mask some absorption bands of easily deuterized groups. Because a similar phenomenon was also observed with compounds (V) and (VI), which have no hydrogen atom α to the nitrile group, but not with compound (II), we may conclude that a series of hydrogen-bonded N-H bands, similar to that reported for imidazole,⁹ is also present in the spectrum of (I), but are noticeable only after deuteration.

C \equiv N Stretching Frequencies.—The amino-nitrile (I) shows C \equiv N absorption at $2232 \pm 7 \text{ cm}^{-1}$ and the hydroxylamine (II) at $2245 \pm 3 \text{ cm}^{-1}$. In general, non-conjugated nitriles absorb in the range ^{10,11} $2250 \pm 10 \text{ cm}^{-1}$, so the frequency of (I) is unusual. Because the intramolecular hydrogen bonding between the hydroxyl and the nitrile group is very weak, as shown by the O-H stretching frequency in dilute carbon tetrachloride solution, the lower value of the nitrile frequency of (I) is hardly ascribable to hydrogen bonding. This is also clear from the nitrile frequencies of some aliphatic nitriles which also have alcoholic hydroxyl groups; these show the ordinary value for saturated alkyl nitriles.¹⁰ In order to study the dipolar structure caused by the lone-pair electrons on the nitrogen adjacent to the nitrile group (cf. certain amines ^{12,13}), several related compounds

TABLE 3.
Frequencies (cm^{-1}) of amino-nitriles.

Amino-nitriles	$\nu(\text{C}\equiv\text{N})$	Amino-nitriles	$\nu(\text{C}\equiv\text{N})$
III; R = Me, R' = H	2227 *	IV'	2212 †
III; R = Et, R' = H	2232 *	Pr ⁿ CH(CN)·NMe ₃ ⁺ I ⁻	2247 †
III; R = Pr ⁿ , R' = H	2227 *	Et ₂ N·CH ₂ ·CN	2232 (in CCl ₄) ¹²
III; R = R' = Me	2219 *		2233 (in CHCl ₃)
III'	2217 *	O<[C ₂ H ₄] ₂ >N·CH ₂ ·CN	2220 (KBr) ¹³
IV	2222 †		

* Liquid film. † Nujol mull.

were examined. Amino-nitriles (III) absorb at $2225 \pm 8 \text{ cm}^{-1}$, but a quaternary ammonium compound, PrⁿCH(CN)·NMe₃⁺I⁻, has a C \equiv N absorption at 2247 cm^{-1} . In the imino-dinitriles (IV) and (IV') the C \equiv N bands are at very low frequencies, 2222 and 2212 cm^{-1} , respectively. Thus the effect of the availability of the nitrogen unshared electrons on the nitrile frequency may be fairly large. A similar reason may explain the difference between the nitrile frequencies of (II) and (IV), since the basic nature of the compounds is quite different. Thus, (II) is only slightly soluble in dilute mineral acids and did not give an acid salt, in contrast to (IV). The low value of the C \equiv N frequency in (I) is therefore probably due to the effect of the nitrogen atom of the hydroxyamino-group, but for some reason the effect of the unshared electrons of the nitrogen in (II) is suppressed.

N-H Deformation Bands.—The band at 1506—1486 cm^{-1} is assigned to $\delta(\text{N-H})$, though the frequency is rather low compared with that assigned for ON-dimethylhydroxylamine⁵ and others.¹² Deuteration helped in this assignment. The low value is probably due to coupling with $\delta(\text{O-H})$ or/and $\nu(\text{C-N})$. As the hydroxylamine (II) has no band in this region, differentiation between (I) and (II) is possible by use of this band.

O-H Deformation Bands.—Deuteration of compounds (I) and (II), and comparison with the compounds (III), (III'), (IV), and (IV') enabled assignment of $\delta(\text{O-H})$ to the

⁹ Anderson, Duncan, and Rossotti, *J.*, 1961, 2165.

¹⁰ Kitson and Griffith, *Analyt. Chem.*, 1952, **24**, 334.

¹¹ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., London, 1958.

¹² Jesson and Thompson, *Spectrochim. Acta*, 1958, **13**, 217.

¹³ Ruske and Ruske, *Chem. Ber.*, 1958, **91**, 2496.

frequencies shown in the Tables. The higher frequency for the compound (I) than that for (II) may be explained by the coupling with $\delta(\text{N-H})$.

Because the O-H deformation frequencies for compounds (II; R = Me, Et, and Pr) are 1409, 1391, and 1390 cm^{-1} ; the weak bands appeared at 2750 and 2770 cm^{-1} are assigned with some confidence to an over-tone of the O-H deformation.

N-O Stretching and C-N-C Skeletal Stretching Frequencies.—As $\nu(\text{N-O})$ band of hydroxylamine and its simple derivatives is located ²⁻⁵ in the region 910—994 cm^{-1} , we examined to well above this frequency.

α -Hydroxyaminopropionitrile shows four distinct bands at 1103 (1090sh), 1014, 960, and 882 cm^{-1} , but as the absorption at 1103 cm^{-1} is absent from the spectra of (V) and (VI), it was not considered here. The two bands at 1014 and 882 cm^{-1} are shifted by deuteration. As the number of carbons in R increases, those bands, except that corresponding to 960 cm^{-1} , split into shoulders or two separate peaks, and decrease in intensity. Compounds (V) and (VI) have five and six bands, respectively, at 1059—894 cm^{-1} , but these are shifted by deuteration, except bands at 914 and 894 cm^{-1} , respectively. The bands affected by deuteration of (V) are either lost or diminished in the case of α -aminoisobutyronitrile.

With compound (II; R = Me) three distinct bands are observed near this region, but none is shifted by deuteration. The middle band is lost in the compound (IV). As the number of carbon atoms in the R increases, the lowest-frequency band splits and decreases in intensity, and new bands appear among the three bands.

The shift of the bands of (I) by deuteration is probably derived from coupling of $\nu(\text{N-O})$ with $\delta(\text{N-H})$ and $\nu(\text{C-N})$.

From consideration of these results and those from NN-dimethylhydroxylamine,⁵ the three bands of the compound (II) in the region were assigned (from high to low frequency) to $\nu_{\text{as}}(\text{C-N-C})$, $\nu(\text{N-O})$, and $\nu_{\text{sym}}(\text{C-N-C})$. When R becomes larger from methyl to hexyl, $\nu_{\text{as}}(\text{C-N-C})$ shifts to higher and $\nu(\text{N-O})$ to lower frequency, and $\nu_{\text{sym}}(\text{C-N-C})$ is split into two, probably because of coupling between the above and the C-C modes.

For compounds (II) having dissimilar R's the spectrum below 1300 cm^{-1} is too complicated to permit assignment.

EXPERIMENTAL

The compounds studied were prepared and purified according to known methods.^{1,14-16} They were deuterated by adding heavy water to a sample dissolved in acetone containing hydrochloric acid, keeping the solution at room temperature, and then evaporating under reduced pressure. All treatments were under nitrogen, and solvents were deoxygenated by bubbling nitrogen through before use. The same procedures were carried out in ordinary water to prove that the decompositions did not take place to an extent detectable spectroscopically. Heavy water was 99.8 weight-% of D_2O , supplied by Showa Denko. Carbon tetrachloride was used in the solution method. Because of poor solubility, 10^{-3}M -solutions of compounds (I) and (II), could not be achieved; saturated solutions were therefore used and the concentration measured. The dilution method was used to test the concentration effect on $\nu(\text{O-H})$. Mulling agents used were Nujol and hexachlorobutadiene. A Hitachi EPI-2, a Hitachi EPI-S2 double-beam prism, and a Koken DS-301 prism spectrophotometer with a sodium chloride cell were used. A 20-mm. cell was used for the dilute carbon tetrachloride solutions.

The authors thank Professor K. Takiura for his interest.

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[Received, May 6th, 1963.]

¹⁴ Zelinsky and Stadnikoff, *Ber.*, 1908, **41**, 2061.

¹⁵ Dubsy, *Ber.*, 1916, **49**, 1049.

¹⁶ Münch, *Ber.*, 1892, **25**, 2070; 1893, **26**, 1552.