Infrared Spectra of Cyclohexanoxime and Cyclohexanoxime-d

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Although several studies have been made on the infrared spectra of oximes, most of them have dealt with OH and C=N stretching vibration. Other vibrational frequencies of the functional group of oximes such as those of the NO stretching, the OH bending, etc. have attracted less attention. The infrared spectra of diacetyl monoxime and isonitrosoacetone have already been reported[1]. The study was undertaken in an attempt to inquire into the character of the absorption spectra of oximes. However, each molecule of these compounds has a carbonyl group in conjugation with a C=N bond. Moreover, the type of hydrogen bondings in these compounds could not be determined uniquely, because both a nitrogen atom and an oxygen atom in an oxime group as well as the oxygen atom of a carbonyl group may take part in hydrogen bonds as a proton acceptor. In the present study, it is attempted to assign the observed bands of cyclohexanoxime and cyclohexanoxime-*d* to various modes of the functional group. These compounds are devoid of conjugate systems. In addition, the crystal structure of cyclohexanoxime has already been determined by X-ray analysis[2]. It is reported that the crystal consists of trimers linked by O–H···N hydrogen bonds. Accordingly, all absorption bands, at least those observed in the spectra of the solid, can be interpreted as arising from the vibrations of assciated molecules linked by hydrogen bonding of this type.

The infrared spectrum of cyclohexanoxime has been recorded by Cross and Rolfe[3], Palm and Werbin[4], Califano and Lüttke[5], Matsui[6] and Bredereck et al.[7], but no complete assignment of bands has been carried out as yet.

Experimental

A commercial preparation of cyclohexanoxime was purified by recrystallization from a solution in ligroin. A deuterated sample was prepared by exchanging hydrogen of OH groups with deuterium from heavy water. These samples were dried before use.

The spectra were taken with a Hilger H-800 spectrophotometer equipped with rock-salt and potassium bromide prisms, the region scanned covering $4000\sim500\ \mathrm{cm}^{-1}$. Both potassium bromide disks and Nujol or hexachlorobutadiene mulls were employed for taking the spectra of solids. Solutions of various concentrations in carbon tetrachloride and carbon disulfide were also used in order to observe changes in absorption intensity with concentration. All the infrared spectra were recorded at room temperature.

Assignment and Discussion

All absorptions associated with the functional group –C=N–OH of oximes except for the C=N stretching vibration are expected to show an appreciable concentration dependence, just as is observed in the spectra of diacetyl monoxime and isonitrosoacetone[1]. On deuteration, new bands arising from OD groups should appear in place of all bands attributable to OH groups. Therefore, attention was paid especially to the concentration dependence of absorption intensity as well as to the disappearance of certain bands on deuteration. Bands involving changes in intensity with concentration are listed in Table I. The C=N stretching frequency is also given in Table I, since it is considered to be a frequency characteristic of the functional group of oximes.

OH and OD Stretching Frequencies, ν(OH) and ν(OD).—For the OH stretching vibration, a single sharp band and a composite broad band consisting of two sub-maxima were observed in the range $3600\sim3000\ \mathrm{cm}^{-1}$ (Fig. 1). The intensity of the latter band became strong with increasing concentration at the expense of that of the former. Only the broad band was present in the spectrum of the solid. These bands shifted towards much lower frequencies on deuteration (Table I). The band of the OD stretching vibration showed a general pattern and a concentration change almost identical with those of the OH stretching

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TABLE I. FREQUENCIES OBSERVED FOR THE FUNCTIONAL GROUP OF CYCLOHEXANOXIME AND CYCLOHEXANOXIME-*d*

Frequency, cm^{-1}		Intensity change on dilution	Assignment
-CNOH	-CNOD		
3598*		increase	ν(OH), free
3250 3115		decrease	ν(OH), assoc.
	2670*	increase	ν(OD), free
	2400	decrease	ν(OD), assoc.
1662	1652	no change	ν(C=N)
1480 A**		decrease	δ(OH), assoc.
1372* B		increase	δ(OH), free
1237* C		increase	δ(OH), free
	1080 A′	decrease	δ(OD), assoc.
	1015* B′	increase	δ(OD), free
	971* C′	increase	δ(OD), free
961 D	955 D′	decrease	ν(NO), assoc.
948* E	944* E′	increase	ν(NO), free
933* F	930* F′	increase	ν(NO), free
795			γ(OH), assoc. (solid)
740*		decrease	γ(OH), assoc. (soln.)
	580		γ(OD), assoc. (solid)
	535*	decrease	γ(OH), assoc. (soln.)

* These bands were not found in the spectra of the solid.
** Some of the peaks in Figs. 2 and 3 are indicated by letters.

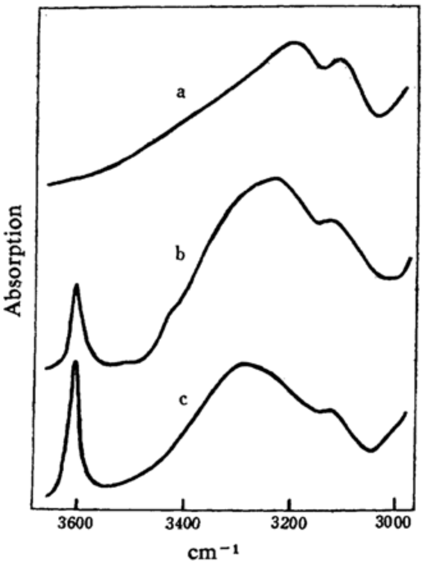

Fig. 1. Infrared absorption spectra of cyclohexanoxime. (a) Solid in a KBr disk, 2 mg./200 mg. KBr. (b) 0.24 mol./l. CCl_4 solution, 0.2 mm. cell. (c) 0.10 mol./l. CCl_4 solution, 0.53 mm. cell.

vibration. However they were masked by the absorption bands of carbon dioxide to such an extent that it was not feasible to locate them exactly. The single sharp band and the broad band were ascribed to the stretching vibrations of the OH or OD bond of free molecules and associated molecules, respectively.

The broad band of bonded OH groups at about 3200 cm^{-1} showed nearly the same appearance regardless of the state of the samples (Fig. 1), indicating that the type of hydrogen bonding formed in solution was -OH···N=C<. The appearance of the band was almost independent of the concentration of solutions. Accordingly, the presence of two sub-maxima in the bonded OH stretching band observed in solutions is not attributable to different kinds of hydrogen bondings or to various polymeric molecules involving hydrogen bondings of various extents. In the spectra of diacetyl monoxime and isonitrosoacetone, similar composite absorptions having few sub-maxima were observed for the bonded OH stretching vibrations. In the previous paper, the form of hydrogen bonding was presumed for these compounds to be of the -OH···O=C< type. However, unlike the behavior of the stretching band of bonded OH groups in cyclohexanoxime, the shape of the bands and the position of the sub-maxima in the spectra of diacetyl monoxime and isonitrosoacetone changed to some extent with the state of aggregation and also with the concentration of solutions. The frequency shift of the OH stretching vibration caused by association was about 240 cm^{-1} in diacetyl monoxime and isonitrosoacetone, whereas it was about 400 cm^{-1} in cyclohexanoxime. This suggests that the hydrogen bonds in cyclohexanoxime are different from and stronger than those in diacetyl monoxime and isonitrosoacetone.

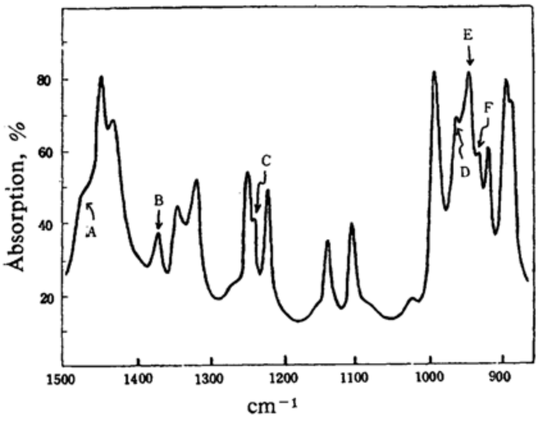

Fig. 2a.

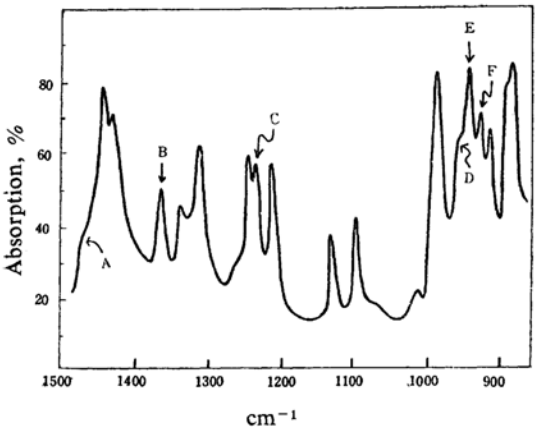

Fig. 2b.

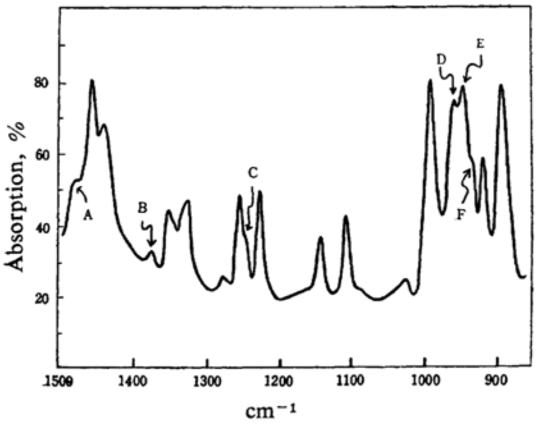

Fig. 2c.

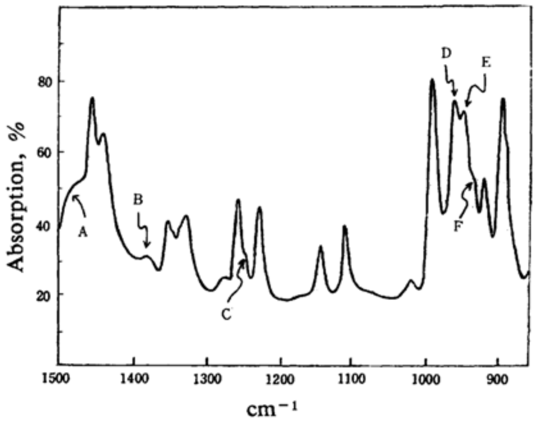

Fig. 2d.

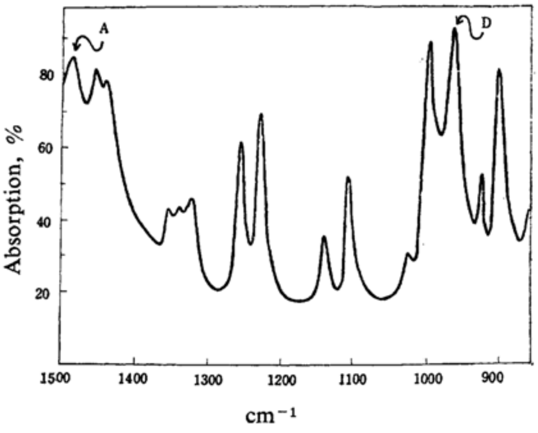

Fig. 2e.

Fig. 2. Infrared absorption spectra of cyclohexanoxime. (a) 0.055 mol./l. CCl_4 or CS_2 solution, 1.6 mm. cell. (b) 0.22 mol./l. CCl_4 or CS_2 solution, 0.4 mm. cell. (c) 0.88 mol./l. CCl_4 solution, 0.1 mm. cell. (d) 1.77 mol./l. CCl_4 solution, 0.05 mm. cell. (e) Solid in a KBr disk, 2 mg./200 mg. KBr.

C=N Stretching Frequency, ν(C=N). — Only one absorption band of medium intensity could be observed in the range 1750~1500 cm^{-1} (Table I). Accordingly, this absorption was assigned to the C=N stretching vibration. The band showed no change in its intensity with concentration and state, although deuteration caused a slight lowering of the frequency.

The value of 1662 cm^{-1} for the C=N stretching vibration is in agreement with 1669 cm^{-1} reported by Cross and Rolfe[3], 1662 cm^{-1} by Palm and Werbin[4] and 1665 cm^{-1} by Bredereck et al.[7] These values are characteristic of unconjugated oximes such as acetaldoxime and formaldoxime and are higher than those of conjugated oximes such as diacetyl monoxime (1630 cm^{-1}) and isonitrosoacetone (1613 cm^{-1}). Since in cyclohexanoxime, diacetyl monoxime and isonitrosoacetone, association caused no frequency shift of the C=N stretching band while deuteration was accompanied by a shift of only about 10 cm^{-1}, a separation between the C=N stretching frequencies of conjugated and unconjugated oximes is presumably due to the difference in the double bond character of the C=N bond. In fact, the C=N bond of *p*-benzoquinone monoxime involving a very strong conjugation absorbs at 1555 cm^{-1}, which is much lower than the corresponding wave number of diacetyl monoxime and isonitrosoacetone[8].

OH and OD In-plane Bending Frequencies, δ(OH) and δ(OD), and Out-of-plane Bending Frequencies, γ(OH) and γ(OD). — Bands disappearing on deuteration and the corresponding bands of the deuterated compound are associated with the absorptions by OH and OD groups, respectively (Table I). Such bands appearing below 1500 cm^{-1} can be classified into two groups on the basis of their frequencies and the widths. One of them includes bands showing a distinct absorption peak in the higher frequency region except for a band at 1480 cm^{-1}, which was partly masked by a strong absorption due to the CH$_2$ bending. The other is comprised of relatively diffuse bands appearing in the lower frequency region. Bands at 1480, 1372 and 1237 cm^{-1} and the corresponding bands of the deuterated compound at 1080, 1015 and 971 cm^{-1} belong to the former group and must be ascribed to the in-plane bending vibration of the OH and OD groups, respectively, because they are in a wave number range, in which this kind of vibration is usually expected (Figs. 2 and 3). The band of cyclohexanoxime near 750 cm^{-1} and that of the deuterated compound at about 550 cm^{-1} belong to the latter group and were assigned to the out-of-plane bending vibration of the OH and OD groups, respectively (Figs. 4 and 5). No absorption band arising from the OH out-of-plane bending vibration of free molecules will be observed in the potassium

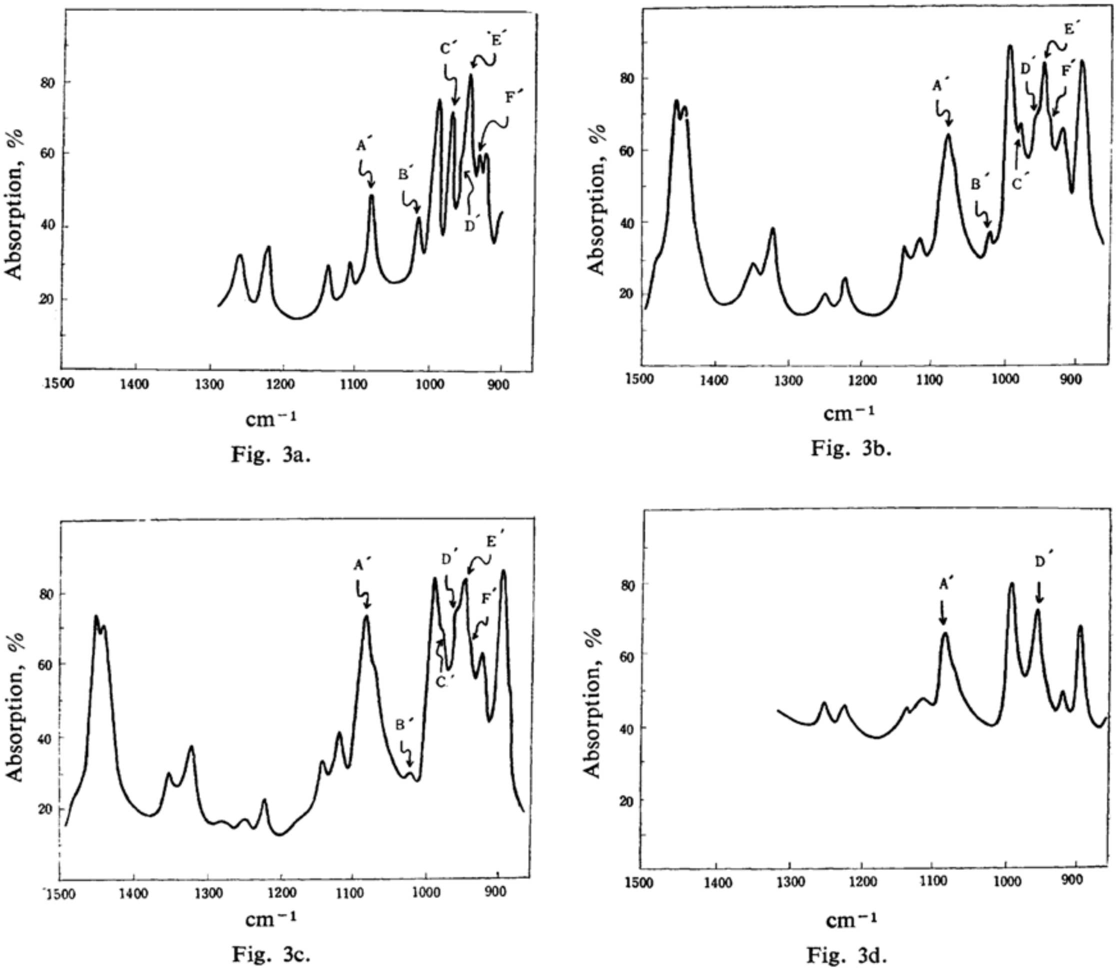

Fig. 3a.

Fig. 3b.

Fig. 3c.

Fig. 3d.

Fig. 3. Infrared absorption spectra of cyclohexanoxime-*d*. (a) 0.035 mol./l. CS$_2$ solution, 1.5 mm. cell. (b) 0.22 mol./l. CCl$_4$ or CS$_2$ solution, 0.5 mm. cell. (c) 0.56 mol. CCl$_4$ solution, 0.2 mm. cell. (d) Solid in a Nujol mull.

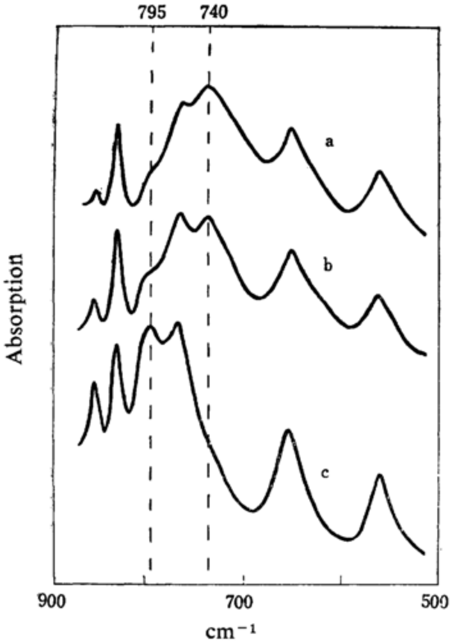

Fig. 4. Infrared absorption spectra of cyclohexanoxime. (a) 0.168 mol./l. CS_2 solution, 0.53 mm. cell. (b) 1.04 mol./l. CS_2 solution, 0.083 mm. cell. (c) Solid in a Nujol mull.

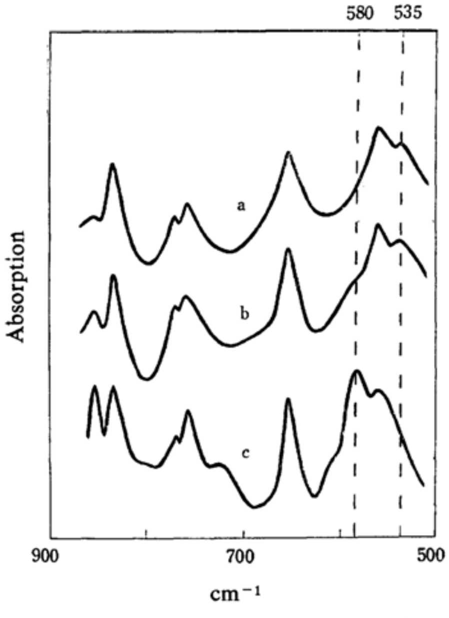

Fig. 5. Infrared absorption spectra of cyclohexanoxime-*d*. (a) 0.168 mol./l. CS_2 solution, 0.53 mm. cell. (b) 1.04 mol./l. CS_2 solution, 0.083 mm. cell. (c) Solid in a Nujol mull.

bromide region. Generally speaking, the OH or OD bending frequency of associated molecules of organic compounds is higher than that of free molecules. Bands arising from free molecules must be absent in the spectra of solids. Thus, the band of cyclohexanoxime at 1480 cm^{-1} and that of the deuterated compound at 1080 cm^{-1} were reasonably assigned to the vibration of associated molecules. This assignment is consistent with the change of intensity with concentration.

Two bands were found to be associated with the OH in-plane bending vibration of free molecules. A similar situation was observed in some alcohols by Tarte and Deponthière[9] and Maclou and Henry[10]. For instance, Tarte and Deponthière have reported two bands at 1243 and 1030 cm^{-1} for ethanol vapor and assigned them to the OH in-plane bending vibration of free molecules, because these bands were replaced by two bands at 890 and 790 cm^{-1} on deuteration. As was pointed out Tarte and Deponthière, two reasons are conceivable for the origin of the appearance of two bands: rotational isomerism about a C–O bond and some coupling such as Fermi resonance. Pritchard and Nelson[11] interpreted the bands of *tert*-butanol in solutions at 1329 and 1141 cm^{-1} as the coupled bands of the CH_3 rocking and the OH in-plane bending of free molecules. However, such coupling seems unlikely to exist in cyclohexanoxime. The ratio of the product of two frequencies for the OH in-plane bending vibration and that for the OD in-plane bending vibration is 1.72 rather than $\sqrt{2}$ as expected from the product rule. The value seems to favor an interpretation of the double band in terms of rotational isomerism about an N–O bond. Such double OH bending frequency was not observed for diacetyl monoxime and isonitrosoacetone. In these compounds, a lower frequency band due to free OH groups might be masked by other strong absorption bands, although it is conceivable that these compounds have a single OH in-plane bending band. Califano and Lüttke did not mention the double character of the free OH bending vibration in their study on acetaldoxime and formaldoxime. Further examination is required in order to elucidate this problem.

Bands at 795 and 580 cm^{-1} observed in the crystals of cyclohexanoxime and cyclohexanoxime-*d*, respectively, could not be observed even in concentrated solutions. However, new very broad bands appeared at 740 and 535 cm^{-1}. The frequency difference between crystals and solutions will be due to the different molecular environments.

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NO Stretching Frequeny, ν(NO).—Bands at 961, 948 and 933 cm^{-1} and the corresponding bands of the deuterated compound at 955, 944 and 930 cm^{-1} can be assigned unequivocally to the NO stretching vibrations (Figs. 2 and 3). From their concentration dependence, it is evident that the band of cyclohexanoxime at 961 cm^{-1} and that of the deuterated compound at 955 cm^{-1} are due to the NO stretching vibration of associated molecules.

Two bands were assigned to the NO stretching vibration of free molecules. They can possibly be ascribed to the respective NO stretching absorptions of two isomers. This fact provides an indirect but additional evidence in favor of the presence of rotational isomers. Deuteration gave rise to a slight shift of the NO stretching frequency to a lower frequency, while association caused a shift to a higher frequency by about 13 cm^{-1}, which is nearly equal to the amount of shift observed in diacetyl monoxime and isonitrosoacetone[1]. The NO stretching frequency observed in the present study is lower than those of *p*-benzoquinone monoxime and naphthoquinone monoximes[8] at about 1000 cm^{-1}, but is much higher than those of alkyl nitrites[12] covering a range 814 ~751 cm^{-1}.

Summary

The infrared absorption bands due to the functional group of cyclohexanoxime and cyclohexanoxime-*d* were reasonably assigned by taking into account the concentration dependence of these bands in solutions. Cyclohexanoxime having no conjugate system showed a spectral feature different in many respects from that of diacetyl monoxime or isonitrosoacetone already studied. The type of hydrogen bonding is $-OH\cdots N=C<$ both in solutions and in the solid state. Consequently, the stretching frequency of bonded OH groups of cyclohexanoxime is different from those of diacetyl monoxime and isonitosoacetone. The doubling of absorption bands was observed for both the OH in-plane bending vibration and the NO stretching vibration of free molecules. This suggests the presence of rotational isomers. The wave numbers of the C=N stretching vibration is higher, while that of the NO stretching vibration is lower than those of the corresponding vibrations of diacetyl monoxime and isonitrosoacetone. This indicates that the double bond character of the C=N bond in cyclohexanoxime is greater than that in oximes having a conjugate system.

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