Infrared Spectra of Diacetyl Monoxime and Isonitrosoacetone

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Oximes are known to be subject to association, which has hampered the elucidation of the molecular structures of this type of compounds by means of physical methods such as dipole moment measurement, etc. The association through hydrogen bonding is an interesting problem in its own right and extensive studies have been made on these compounds by means of infrared spectroscopy[1] and Raman effect and also by the freezing point depression[2] of solutions, X-ray analysis[3-6] on crystals, etc. For this purpose, it is desirable and even necessary to carry out as complete assignments as possible of observed frequencies to various modes of vibrations of characteristic groups. Two oximes having conjugated double bonds were chosen in the present study anticipating the possible increase of the effect of hydrogen bonding due to conjugation.

Materials

Diacetyl Monoxime.—A commerical preparation was purified by recrystallization from an aqueous solution (m. p. 74.5°C).

Isonitrosoacetone.—A commercial sample was purified by extraction from an ether solution with petroleum ether (m. p. 64.5°C).

Experimental

The infrared spectra were recorded with a Hilger H-800 infrared spectrophotometer equipped with a rock-salt prism as well as with a fluorite prism. Both these compounds were studied in carbon tetrachloride and in carbon bisulfide, no appreciable dependence of frequencies upon the kind of solvents being observed. For isonitrosoacetone, which was sparingly soluble in carbon tetrachloride and carbon bisulfide, also chloroform solutions were employed. The results are shown in Tables I and II.

The spectra of solutions of various concentrations, solid samples, and some of the deuterated compounds, CH_3-CO-CR-NOD (R=CH_3 or H), were also studied whenever they were required for carrying out assignments.

Discussion

The spectra of diacetyl monoxime and isonitrosoacetone in the wave number range from 3200 to 3600 cm^{-1} are reproduced in Figs. 1 and 2. They show a very strong sharp band at about 3570 cm^{-1} and a broad band at about 3330 cm^{-1}. The intensity of the former decreases, whereas that of the latter increases with increasing concentration. The former disappears completely in the solid state. These bands are absent in the spectra of the corresponding deuterated compounds, which display a new strong sharp band at about 2620 cm^{-1} along with a broad band at about 2470 cm^{-1}. These facts indicate that the band of diacetyl monoxime at 3577 cm^{-1} and that of isonitrosoacetone at 3574 cm^{-1} can be unequivocally assigned to the OH stretching vibration of free OH groups, while the band of the former compound at about 3345 cm^{-1} and that of the latter at about 3325 cm^{-1} can be assigned to the OH stretching vibration of hydrogen-bonded OH groups. These wave numbers suggest that

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[1] A. M. Buswell, W. H. Rodebush and M. F. Roy, *J. Am. Chem. Soc.*, **60**, 2444 (1938).

[2] A. Reiser, Symposium on Hydrogen Bonding held in Ljubljana, 1957. See also D. Hadži and H. W. Thompson, "Hydrogen Bonding", Pergamon Press, London (1959), p. 443.

[3] T. K. Bierlein and E. C. Lingafelter, *Acta Cryst.*, **4**, 450 (1951).

[4] Y. Okaya, A. Shimada and I. Nitta, This Bulletin, **29**, 210 (1956).

[5] D. E. Williams, G. Wohlauer and R. E. Rundle, *J. Am. Chem. Soc.*, **81**, 755 (1959).

[6] L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

TABLE I. INFRARED ABSORPTION OF DIACETYL MONOXIME

Wave number cm^{-1}	Intensity	Assignment
3577	strong	OH stretching (free)
3345	strong, very broad	OH stretching (assoc.)
3065	weak, broad	CH_3 degenerate stretching
2945	weak, broad	CH_3 symmetric stretching
1698	strong	CO stretching (free)
1686	shoulder	CO stretching (assoc.)
1630	weak	CN stretching
1424	medium, broad	CH_3 degenerate deformation
1365	strong	CH_3 symmetric deformation
1355	strong	OH in-plane bending (free)
1304	weak	CC(central) stretching (assoc.)
1298	weak	CC(central) stretching (free)
1124	strong	CH_3 in-plane rocking
1022	strong	CH_3 in-plane rocking
970	weak	NO stretching (assoc.)
963	weak	NO stretching (free)
933	weak	C–CH_3 stretching

TABLE II. INFRARED ABSORPTIONS OF ISONITROSOACETONE

Wave number cm^{-1}	Intensity	Assignment
3574	strong	OH stretching (free)
3325	strong, broad	OH stretching (assoc.)
1703	strong	CO stretching (free)
1674	strong	CO stretching (assoc.)
1614	medium	CN stretching
1450	medium	CH_3 degenerate deformation
1398	strong	OH bending (free)
1366	strong	CH_3 symmetric deformation
1320	very weak	CC(central) stretching
1226	strong	CH in-plane bending
1016	strong	CH_3 in-plane rocking
990	strong	NO stretching (assoc.)
972	strong	NO stretching (free)
920	medium	C–CH_3 stretching
835	weak	CH out-of-plane bending

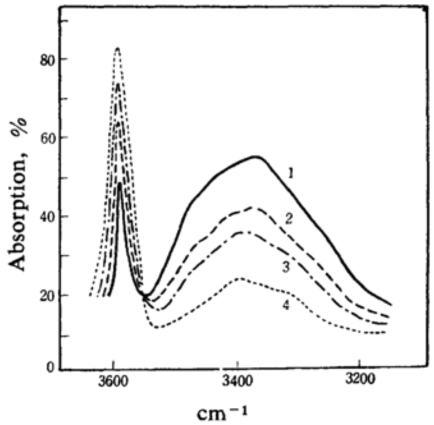

Fig. 1. Diacetyl monoxime in carbon tetrachloride.
1) 0.312 mol./1., 0.010 cm. cell. 2) 0.078 mol./1., 0.040 cm. cell. 3) 0.039 mol./1., 0.080 cm. cell. 4) 0.010 mol./1., 0.320 cm. cell.

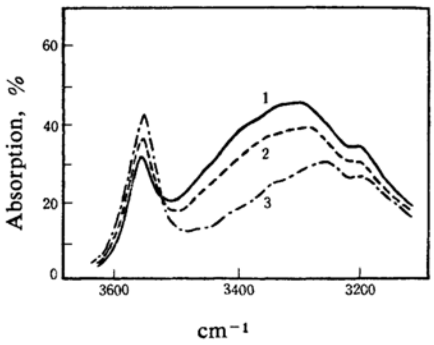

Fig. 2. Isonitrosoacetone in chloroform.
1) 0.901 mol./1., 0.002 cm. cell. 2) 0.340 mol./1., 0.004 cm. cell. 3) 0.021 mol./1., 0.064 cm. cell.

intermolecular hydrogen bondings are involved in association, because the stretching vibration of OH groups forming a chelate ring is known⁷⁾ to absorb at a frequency much lower than 3300 cm^{-1}.

The value of about 3570 cm^{-1} for the wave number of stretching vibration of free OH groups is fairly low compared with those of alcohols ranging in 3600∼3650 cm^{-1} and is rather close to those of carboxylic acids at about 3600 cm^{-1}. Oximes having no conjugate double bonds, such as acetaldoxime, acetoxime, cyclohexanoxime, etc.⁸⁾ absorb at about 3600 cm^{-1} in solutions, while those containing conjugate double bonds show absorptions at lower frequencies. For instance, benzaldoxime and its derivatives absorb in the wave number range 3500∼3560 cm^{-1} in solutions,* and quinone monoxime¹⁰⁾ at 3540 cm^{-1}. The present results are consistent with this relation. On the other hand, the values of 3345 cm^{-1} and 3325 cm^{-1} for the wave numbers of stretching vibrations of hydrogen-bonded OH groups of the two compounds under investigation are higher than those of the oximes mentioned above, most of which absorb at a wave number lower than 3300 cm^{-1}**.

Three types of hydrogen bonds can be presumed, namely $-\mathrm{OH}\cdots\mathrm{N{=}C}$, $-\mathrm{OH}\cdots\mathrm{O{-}N{=}}$ and $-\mathrm{OH}\cdots\mathrm{O{=}C{-}}$. The type of association will be discussed below in connection with other absorption bands. As can be anticipated, Raman spectra show no line corresponding to OH stretching vibration or only a very weak line¹¹,¹²⁾.

The weak broad bands at 3065 and 2945 cm^{-1} of diacetyl monoxime were assigned to the degenerate and symmetric stretching vibrations of methyl groups, respectively. The appearance of these bands observed in solutions were not altered appreciably on solidification or on deuteration. The corresponding bands and the CH stretching vibration of isonitrosoacetone were too weak to be observed with certainty. Therefore, they are not listed in Table II.

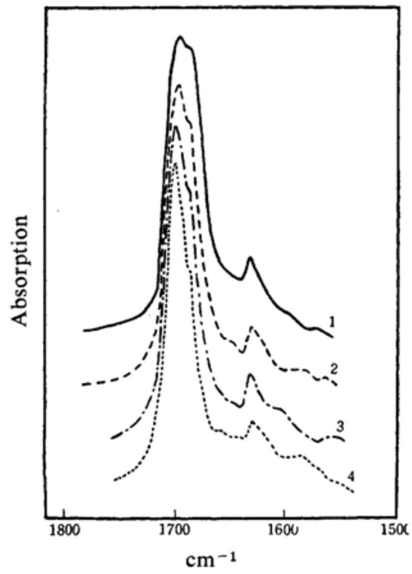

Fig. 3. Diacetyl monoxime in carbon tetrachloride.
1) 0.312 mol./l., 0.010 cm. cell. 2) 0.078 mol./l., 0.040 cm. cell. 3) 0.039 mol./l., 0.080 cm. cell. 4) 0.020 mol./l., 0.160 cm. cell. In this and subsequent figures, the ordinates of curves are shifted from one another for the sake of clarity.

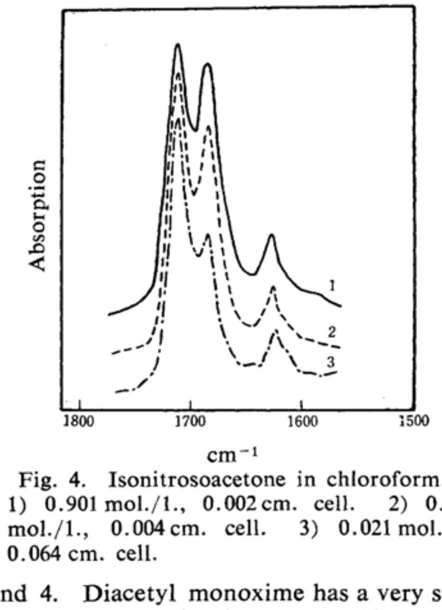

Fig. 4. Isonitrosoacetone in chloroform.
1) 0.901 mol./l., 0.002 cm. cell. 2) 0.340 mol./l., 0.004 cm. cell. 3) 0.021 mol./l., 0.064 cm. cell.

The spectra in the wave number range covering 1600∼1700 cm^{-1} are shown in Figs. 3 and 4. Diacetyl monoxime has a very strong band at 1698 cm^{-1} with a shoulder at 1686 cm^{-1}. The corresponding band of isonitrosoacetone split into two peaks, a main peak being found at 1703 cm^{-1} and a subsidiary one at 1674 cm^{-1}. Besides, a relatively weak band appeared at 1630 cm^{-1} in the spectrum of diacetyl monoxime and at 1614 cm^{-1} in that of isonitrosoacetone. The general features of these bands were not affected by deuteration, except for slight changes taking place in the

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7) L. J. Bellamay, "The Infrared Spectra of Complex Molecules", 2nd Ed., Methuen, London (1958).

8) S. Califano and W. Lüttke, *Z. physik. Chem.* (neue Folge), **5**, 240 (1956).

9) A. Palm and H. Werbin, *Can. J. Chem.*, **31**, 1004 (1953).

10) D. Hadži, *J. Chem. Soc.*, **1956**, 2725.

* The values of wave numbers observed by Palm and Werbin⁹⁾ are distributed over a wide range, no characteristic tendency being found for the present.

** Califano and Lüttke⁸⁾ reported a value of 3315 cm^{-1} for *syn*-benzaldoxime, while Palm and Werbin⁹⁾ observed a band at 3270 cm^{-1} for β(*anti*)-benzaldoxime in a chloroform solution.

11) M. Milone, *Gazz. chim. ital.*, **67**, 527 (1937).

12) L. Kahovec and K. W. F. Kohlrausch, *Ber.*, **75**, 1541 (1942).

position of absorption bands. In general, saturated open chain ketones absorb in the range of 1705~1725 cm^{-1}, while compounds having a C=N bond show an absorption in the range of 1640~1690 cm^{-1}, provied that the compounds have an open chain or that they have a ring system involving no conjugation. Although the frequencies of CO and CN stretching vibrations may shift to some extent in conjugate systems, it is still reasonable to presume that the CO stretching vibration has a higher frequency than that of the CN stretching vibration. In addition, a band due to the CO stretching vibration is, in general, very strong, whereas a band due to the CN stretching is not always so. For these reasons, the bands at about 1700 cm^{-1} were assigned to the CO stretching vibration and those at about 1620 cm^{-1} to the CN stretching mode.

Kahovec and Kohlrausch[12] observed two Raman frequencies, 1679 and 1632 cm^{-1}, of diacetyl monoxime in the crystalline state. They tentatively assigned these frequencies to the CO stretching and the CN stretching vibration, respectively, with due precaution to the low value of the latter frequency compared with those of acetaldoxime, etc.[11,13,14] at about 1670 cm^{-1}. Their assignments seem to be adequate, because strong conjugation in a molecule will lower the characteristic frequency associated with a double bond. In fact, Hadži[10] observed the CO band of 1,4-benzoquinone monoxime at 1628 cm^{-1} in the solid state and at 1648 cm^{-1} in solutions and also the CN band at 1555 cm^{-1} in the solid state. Palm and Werbin[9] have made observations on the CN frequencies of benzaldoxime and its derivatives in the solid state, the observed values ranging from 1614 to 1650 cm^{-1}.

The CO bands mentioned above showed a decrease in intensity of the main peak and an increase in that of the subsidiary peak or the shoulder with increasing concentration. The effect of association on the CO stretching frequency is presumed to cause a shift towards a lower frequency owing to the increased single bond character of the C=O bond due to hydrogen bond formation. Accordingly, the main peaks were assigned to the stretching vibration of free CO groups while the subsidiary peak and the shoulder were assigned to that of hydrogen-bonded CO groups. This suggests that hydrogen bonds of the -OH$\cdots$O=C- type are present in solutions.

The absorption spectrum of diacetyl monoxime in the wave number range 1300~1500 cm^{-1} is shown in Fig. 5. A band at about 1424 cm^{-1} is a broad one of medium intensity. A strong band 1365 cm^{-1} had a shoulder, which changed into a distinct maximum at 1355 cm^{-1} with increasing dilution. The same compound in the solid state showed a broad band at about 1430 cm^{-1} and a sharp one at 1365 cm^{-1}, no peak or shoulder being observed at about 1355 cm^{-1}. The change of spectral features taking place on deuteration was inappreciable, except that the band at 1355 cm^{-1} disappeared and a new band appeared at about 1000 cm^{-1}, although it overlapped with other bands. Based on these experimental facts, the band at 1355 cm^{-1} was assigned to the bending vibration of free OH groups. Palm and Werbin[15] proposed to assign a band of α(*syn*)-benzaldoxime at 1265 cm^{-1} to the OH in-plane bending vibration, Hadži[10] assigned a band of quinone oxime near 1450 cm^{-1} to the OH bending vibration, and Bratož et al.[16] found the values of 1460 and 1078 cm^{-1} for the OH and OD bending vibrations, respectively. These results suggest the adequacy of the present assignments.

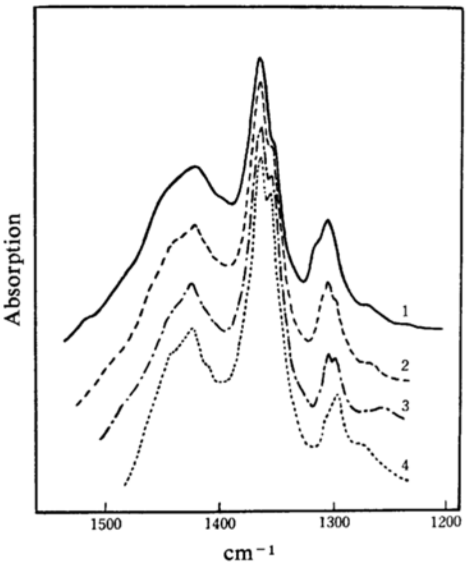

Fig. 5. Diacetyl monoxime in carbon tetrachloride.

The concentrations and the cell lengths are the same as given in Fig. 3.

Two bands at 1424 and 1365 cm^{-1} mentioned above were assigned to the CH$_3$ degenerate and symmetric deformation vibrations, respectively, because they showed no concentration change and also because they were not affected by deuteration. The slight decrease of these frequencies below those of hydrocarbons is presumed to be a result of the presence of a C=O or C=N group in the molecule. In fact,

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[13] J. Goubeau, ibid., **68**, 912 (1935).

[14] H. J. Bernstein and W. H. Martin, *Trans. Roy. Soc. Canada*, Sect. III, **31**, 105 (1937).

[15] A. Palm and H. Werbin, *Can. J. Chem.*, **32**, 858 (1954).

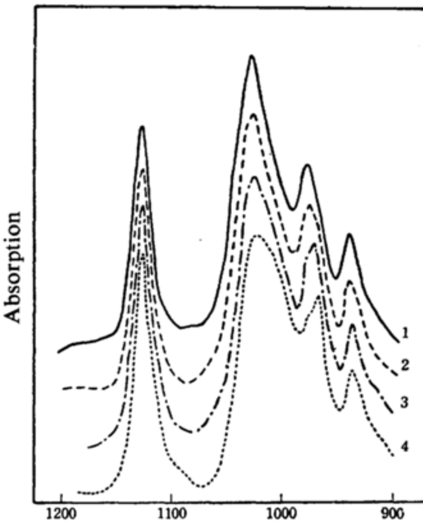
[16] S. Bratož, D. Hadži and G. Rossmy, *Trans. Faraday Soc.*, **52**, 464 (1956).

acetone[17] shows absorptions at 1430 and 1363 cm^{-1} and diacetyl at 1426 and 1362 cm^{-1} in the vapor state and at 1420 and 1352 cm^{-1} in the liquid state[18,19]. The Raman frequencies of diacetyl monoxime observed by Kahovec and Kohlrausch[12] correspond to these vibrational modes. The OH bending frequency of hydrogen-bonded OH groups was not observed clearly but, as suggested also by Califano and Lüttke[20] in their studies on formaldoxime and acetoxime, is expected to be masked by the band at 1424 cm^{-1}. In fact, this band became relatively weak and sharp with decreasing concentration as well as on deuteration.

Another band at about 1300 cm^{-1} appeared to consist of two component peaks at 1304 and 1298 cm^{-1}. The former was stronger than the latter in concentrated solutions, whereas the intensity relation was reversed in dilute solutions. Accordingly, by taking into account the weak intensity of the band and the value of the wave number, the former was assigned to the C–C(central) stretching vibration of associated molecules, while the latter was assigned to that of unassociated ones. The increase of frequency displayed by associated molecules over that of unassociated ones can be readily explained, since the C–C bond in an associated molecule has a greater double bond character than the bond has in an unassociated molecule. This rather weak band due to the C–C stretching vibration has its counterpart in the Raman spectra observed by Kahovec and Kohlrausch[12], who observed a very strong Raman band at 1310 cm^{-1} in a chloroform solution and at 1315 cm^{-1} in the crystalline state. The value of 1300 cm^{-1} is fairly large for a C–C stretching vibration, but is nearly equal to 1284 cm^{-1} observed in the Raman spectra of diacetyl involving also the conjugation of double bonds[18,19].

In this wave number range, isonitrosoacetone absorbed in much the same way as diacetyl monoxime did. The spectra of the former differed from that of the latter only in that the absorption frequency due to the OH bending vibration at 1398 cm^{-1} and that due to the CH_3 degenerate deformation vibration overlapped each other. Accordingly, the latter was evaluated from the spectra of the solid or of the deuterated sample. The same precaution was also taken for the C–C stretching vibration, because it was very weak.

The vibrational modes expected to appear in the wave number range 800∼1250 cm^{-1} are CH_3 in-plane and out-of-plane rocking vibrations, an NO stretching vibration, a C–CH_3 stretching vibration and an OH out-of-plane bending vibration. Isonitrosoacetone will show additional bands due to the CH in-plane and out-of-plane bending motions. Only a band arising from the NO stretching vibrations is possibly subject to an intensity change with concentration. A band having such a character was observed at 963∼970 cm^{-1} for diacetyl monoxime (See Fig. 6.) and at 972∼990 cm^{-1} for isonitrosoacetone.



cm^{-1}

Fig. 6. Diacetyl monoxime in carbon tetrachloride.

1) 0.397 mol./l., 0.008 cm. cell. 2) 0.198 mol./l., 0.016 cm. cell. 3) 0.099 mol./l., 0.032 cm. cell. 4) 0.060 mol./l., 0.053 cm. cell.

The double bond character of the N–O bond will be greater in associated molecules than in unassociated ones. Accordingly, the increase in the amount of associated molecules with increasing concentration will give rise to an increase in the intensity of the component peak of higher frequency. This explains adequately the results of observations that with increasing dilution the maximum of these composite bands shifted towards the longer wavelength side. Hadži[10] assigned a band of 1, 4-benzoquinone monoxime at 1025 cm^{-1} while Palm and Werbin[15] assigned the bands of various oximes at about 940 cm^{-1} to the NO stretching vibration. The present assignment is in agreement with theirs.

A weak band of diacetyl monoxime at 933 cm^{-1} and that of isonitrosoacetone at 920 cm^{-1} were assigned to the C–CH_3 stretching vibration, reference being directed to a similar band of diacetyl at 945 cm^{-1}.

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[17] D. Price, *J. Chem. Phys.*, **9**, 725 (1941).

[18] T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 743 (1953).

[19] J. W. Sidman and D. S. McClure, *J. Am. Chem. Soc.*, **77**, 6471 (1955).

[20] S. Califano and W. Lüttke, *Z. physik. Chem.* (neue Folge), **6**, 83 (1956).

Isonitrosoacetone showed an absorption at 833 cm^{-1}, which had no counterpart in the spectrum of diacetyl monoxime. For this reason and also because the frequencies of out-of-plane vibrations are known to be lower than those of in-plane vibrations, this band was assigned to the CH out-of-plane bending vibration.

Bands still left to be assigned are those of diacetyl monoxime at 1124 and 1022 cm^{-1} and of isonitrosoacetone at 1226 and 1016 cm^{-1}. Since CH in-plane bending vibrations usually absorb at higher frequencies than CH_3 in-plane rocking vibrations do, the band at 1226 cm^{-1} was assigned to the CH in-plane bending mode and others to the CH_3 rocking modes.

For both diacetyl monoxime and isonitrosoacetone, the band near 1020 cm^{-1}, which was sharp in the solid state, showed a hump on the lower frequency side especially in dilute solutions. This suggests the presence of another band capable of being assigned to the OH out-of-plane bending vibration of unassociated molecules.

In this way, all major observed bands have been interpreted in terms of the molecular form of an oxime type, $CH_3-CO-CR=NOH$ ($R=CH_3$ or H). If the molecules exist in a nitroso form, $CH_3-CO-CHR-NO$, bands ascribed to hydroxyl groups in the present investigation could hardly be explained adequately. In addition, the presence of a C–N bond and an N=O bond in a molecule of the nitroso form in place of a C=N bond and an N–O bond as in that of the oxime form will render proper assignments almost impossible. The coexistence of the two forms is also ruled out, because the spectra are simpler than might be expected for the presence of the two forms. This conclusion affords at least an element of simplification in dealing with these molecules by means of other physical methods of attack.

Summary

The infrared absorption spectra of diacetyl monoxime and isonitrosoacetone in solutions were recorded in the rock-salt region. The assignment of observed bands was carried out, taking into account the concentration dependence of the spectra, the effect of deuteration, and the absorptions in the solid state. All the observed frequencies could be interpreted in terms of the molecular form of an oxime type, the presence of molecules in a nitroso form being presumed to be unlikely.

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