536. *Infrared Spectra and Structure of Some Quinone Monoximes.*

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Infrared spectra have been investigated for the monoximes of *p*-benzoquinone and 1 : 4- and 1 : 2-naphthaquinone (both isomers) as well as of their deuterium-substitution products. It has been found that the oxime formulation correctly represents the structure of these compounds in the solid state, and that this structure predominates also in their chloroform solutions. However, 1 : 2-naphthaquinone 2-oxime seems to exist in the (chelated) nitroso-form in solution in carbon tetrachloride. Probable assignments have been made of the C=O, C=N, and N–O stretching bands and the OH deformation band. The O–H stretching frequencies are discussed in connection with hydrogen bonding.

Recently, it has been shown by Havinga and his associates [1] on the basis of electronic spectra that *p*-nitrosophenol exists in solution as the phenol along with the quinone oxime whereas it seems to be in the latter form only in the solid state. The same authors have found 1 : 4-naphthaquinone oxime to be the predominating tautomer in solution. Burawoy and his associates [2] have similarly shown that *o*-benzoquinone oxime forms solutions in which the phenolic tautomer prevails, but that 1 : 2-naphthaquinone 1-oxime exists in this form only. Jaffé [3] has calculated by the molecular-orbital method that the oxime form of *p*-nitrosophenol should be the more stable.

The present investigation aims at assigning some of the characteristic infrared bands for this group of compounds, besides bringing additional evidence as to their structure, particularly in the solid state. Special interest is paid to the OH bands and to hydrogen bonding. It includes the spectra of the deuterated monoximes of 1 : 4-benzoquinone and of 1 : 4- and 1 : 2-naphthaquinones, and of the normal compounds. The spectra of some of the oxime ethers and metallic derivatives were recorded for reference, but will not be discussed in detail here.

Region between 1700 *and* 700 K (= cm.$^{-1}$)*.—The spectra of the quinone oximes have certain features in this region in common, two of which in particular may be used as evidence of structure. The quinone oxime structure requires the presence of a band due to the C=O stretching mode, which (see Fig. 1) is between 1618 and 1668 K in the spectra of solids, and between 1632 and 1680 K in the spectra of chloroform solutions. The wave numbers of

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* For use of K (Kayser) for cm.$^{-1}$ see Editorial Report on Nomenclature, *J.*, 1955, 4497.

[1] Schors, Kraaijeveld, and Havinga, *Rec. Trav. chim.*, 1955, **74**, 1243.

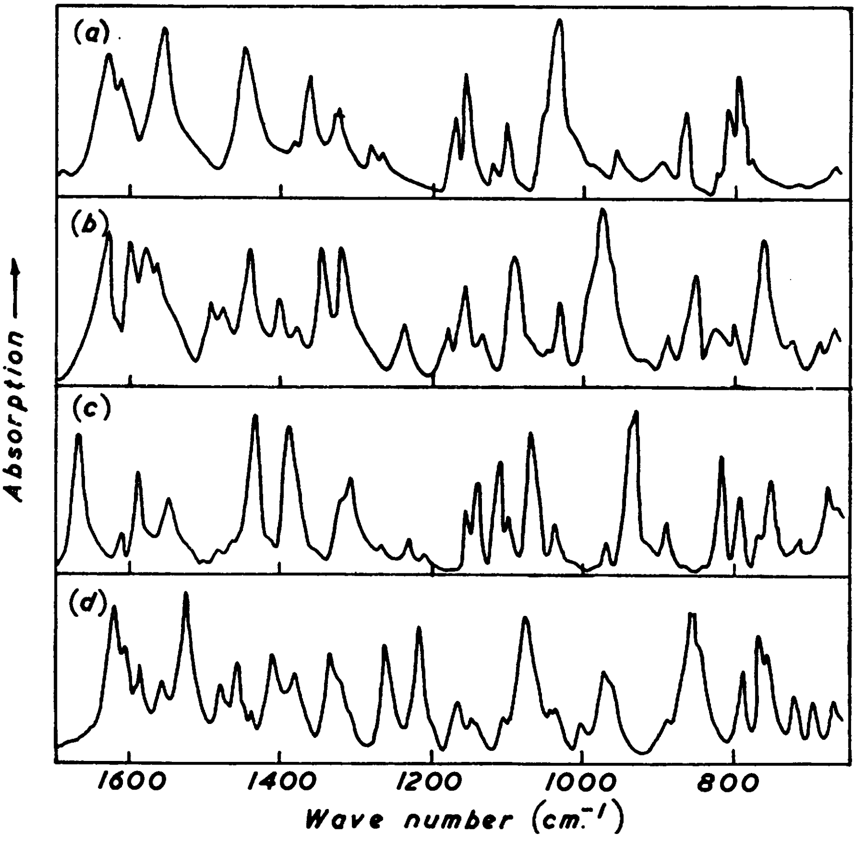
[2] Burawoy, Cais, Chamberlain, Liversidge, and Thompson, *J.*, 1955, 3727.

[3] Jaffé, *J. Amer. Chem. Soc.*, 1955, **77**, 4448.

the C=O bands of the oximes in solution are not much different from those for quinones[4] (benzoquinone 1667; 1 : 4- 1675, and 1 : 2-naphthaquinone 1678 K). A point for comparison is also the wave numbers of the C=O bands of the oxime ethers: with 1 : 2-naphthaquinone 1-oxime ether it is 1660 K, and with the 2-oxime ether 1670 K (both solid). The extremely small wave number of the carbonyl stretching band of 1 : 2-naphthaquinone 1-oxime is due to chelation, which is shown also by the OH stretching band (discussed below).

The oxime structure requires also a C=N stretching band. In the spectra of simpler oximes,[5] this appears between 1618 and 1660 K, which is slightly lower than the position of the corresponding carbonyl band. Strong bands with even smaller wave numbers (1520—1570 K) are found in the quinone oxime spectra as well as in the spectra of the two oxime ethers investigated, but are absent from the spectra of the corresponding quinones. Thus they may be associated to some extent with the C=N group, and their small wave numbers explained in terms of a strong conjugation with the quinonoid double bonds, particularly the C=O group, and subsequent reduction of the double-bond character of the C=N bond. It is interesting to note that the C=N bands in the spectra of aromatic aldoximes and ketoximes tend to be weak,[5] whereas the bands now discussed are strong. This is probably due to an increase in bond polarity owing to conjugation. However, a motion of the hydroxylic group seems also to participate in the vibration mode giving rise to the bands

FIG. 1. *Infrared spectra of: benzoquinone monoxime (A); 1 : 4-naphthaquinone monoxime (B); 1 : 2-naphthaquinone 2-oxime (C), and 1 : 2-naphthaquinone 1-oxime (D). (Solids, mulled.)*



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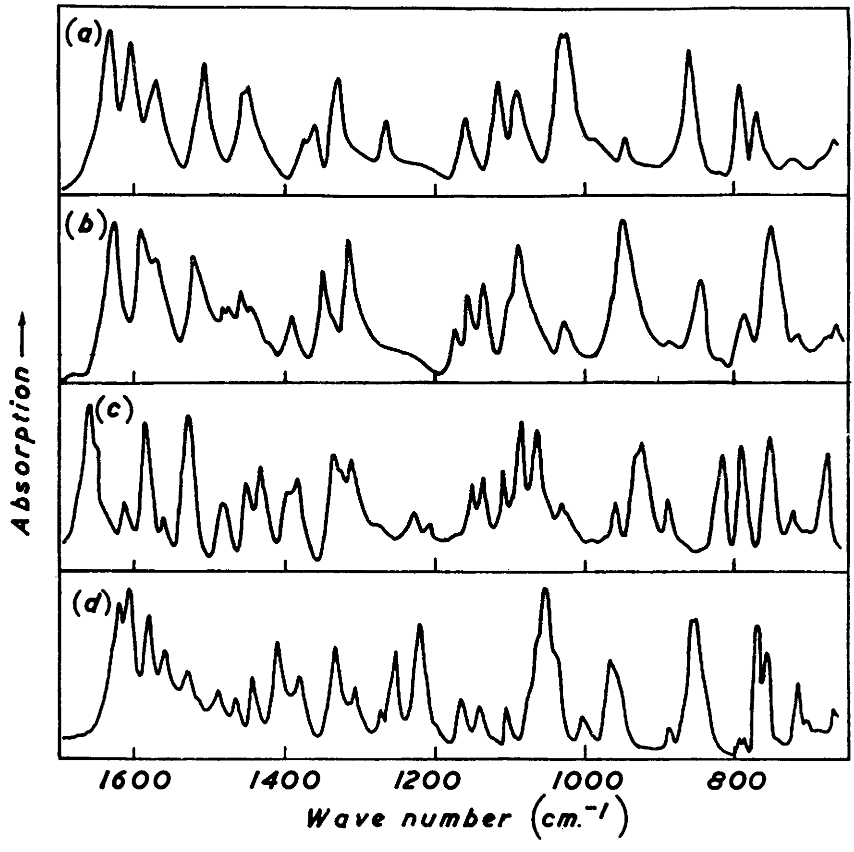
[4] Josien, Fuson, Lebas, and Gregory, *J. Chem. Phys.*, 1953, **21**, 331.

[5] Palm and Werbin, *Canad. J. Chem.*, 1953, **31**, 1004; Duyckaerts, *Bull. Soc. roy. Sci. Liège*, 1952,

near 1550 K. This follows from the observed small shift of these bands to smaller wave numbers after substitution by deuterium (cf. Fig. 2), *e.g.*, in benzoquinone oxime from 1555 to 1508 K, and in 1 : 4-naphthaquinone oxime from 1562 to 1518 K. Smaller shifts on deuteration are observed also with the C=O band. The probable cause of these shifts is the interaction of the vibrations of the double bonds with the in-plane deformation vibration of the hydroxyl group. Both vibrations are of the in-plane type and have similar frequencies, as will be shown further below, and can thus interact.[6] A number of cases of the interaction of bending vibrations of the hydroxyl group with other vibrations having similar frequencies and belonging to the same symmetry type have been observed.[7,8,9] A band which might be connected with the OH bending mode is the strong one appearing near 1440 K. It is strongly reduced on deuteration and is weaker also in the spectra of solutions. Bands due mainly to the OH bending have been observed previously in this region,[7,8,10] but have smaller wave numbers for simple oximes [11] and hydroxylamine itself.[12] However, in hydroxylamine hydrochloride, a band at 1563 K has been assigned to this mode.[12] If 1440 K is taken as the position of the δOH band in the quinone oxime spectra, the corresponding δOD band may be expected to appear near

FIG. 2. *Deuterated quinone monoximes. Letters refer to analogous compounds as in Fig.* 1.



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[6] Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. van Nostrand Co., New York, 1946, p. 194.

[7] Hadži and Sheppard, *Proc. Roy. Soc.*, 1953, *A*, **216**, 247.

[8] Bratož, Hadži, and Rossmy, *Trans. Faraday Soc.*, 1956, **52**, 464.

[9] Mecke and Rossmy, *Z. Elektrochem.*, 1955, **59**, 866.

[10] Giguère and Olmos, *Canad. J. Chem.*, 1952, **30**, 821.

[11] Palm and Werbin, *ibid.*, 1954, **32**, 858.

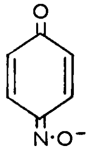
[12] Giguère and Liu, *ibid.*, 1952, **30**, 948.

1100 K. In the spectra of deuterated benzoquinone oxime and 1 : 2-naphthaquinone 2-oxime there are new bands at 1092 and 1086 K, respectively, and they may be assigned to the δOD mode. The situation is less clear in the case of 1 : 4-naphthaquinone oxime, in the spectrum of which this band seems to coincide with a strong one at 1100 K, and appears as a shoulder on the side of larger wave numbers. Similarly, in the spectrum of deuterated 1 : 2-naphthaquinone 1-oxime, only a shoulder on the strong band at 1055 K is observed. This compound differs from the others also in that the presumed δOH band at 1455 K is weak, and that no substitute with smaller wave numbers appears on deuteration for the disappearing band at 1526 K. However, this compound differs from the rest in the type of hydrogen bonding, as will be shown below, and this might explain also the different appearance of the δOH band.

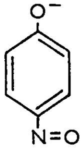
It is interesting that δOD bands have been found [9] between 930 and 970 K in the spectra of associated phenols, which is considerably lower than in the present case. It has been suggested [8] that the position of the δOD band is characteristic of the type of compound to a certain degree, and therefore the assignment of the band near 1100 K to this vibration mode makes the phenolic nature of the hydroxyl improbable in the compounds investigated, in agreement with the oxime structure proposed.

Another strong and characteristic feature in the spectra of quinone oximes appears between 975 and 1075 K. This band is shifted slightly for solutions but more so in some cases after deuteration. It is found within the above limits also in the two spectra of the oxime ethers. Consequently, it is assigned to the N–OH stretching, although it appears to have a slightly larger wave number than in the spectra of other compounds containing this group. In particular, it has been found [11] between 927 and 957 K in the spectra of simple oximes. In the case of 1 : 2-naphthaquinone 2-oxime, two alternatives exist for the assignment to the N–O stretching band, *i.e.*, 932 and 1069 K. Although the former is stronger and shows a slightly larger shift after deuteration, the latter is assigned to the N–O group on following grounds: In the spectra of the sodium and the potassium salts of quinone oximes, the N–O bands are expected to have larger wave numbers because of the resonance between structures (I) and (II), enhancing the double-bond character of this bond. In fact, strong bands are found in the salts of both 1 : 2-naphthaquinones near 1200 K instead of the bands near 1070 K in the spectra of the original oximes, whereas the band near 930 K appears also in the salts of 1 : 2-naphthaquinone 2-oxime.

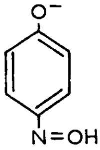
The relatively large wave numbers of the N–O stretching bands in the present cases may be explained, together with the relatively small wave numbers of the C=O and C=N bands, by a considerable contribution of structures of the type (III).



(I)



(II)



(III)

The effect of this type of structure is increased by hydrogen bonding, and this is reflected in the considerable shift of the N–O band towards smaller wave numbers in the spectra of solutions (Table 1).

The spectra of the quinone oximes contain several strong bands in the region between 700 and 900 K. They belong mainly to the out-of-plane vibrations of hydrogen atoms. Although the γ-CH bands are characteristic of the type of substitution in aromatic and unsaturated compounds, no additional evidence of the structure could be drawn in the present cases. A comparison between the spectra of appropriately substituted benzene and naphthalene derivatives with quinones failed to show a reliable point of distinction. This result is not surprising, since in both types of structures the number of adjacent hydrogen atoms is the same, and this is important for the appearance of the γ-CH bands.[13]

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[13] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.

In this spectral region the γ-OH band (out-of-plane deformation mode) is also expected to appear. It may be identified with the bands at 890 and 825 K in the spectra of benzoquinone oxime and of 1 : 4-naphthaquinone oxime, respectively, since these bands disappear on deuteration. The band at 770 K in the spectrum of naphthaquinone 2-oxime seems to have rather small a wave number, but there is no other band in the neighbourhood to disappear on deuteration. There is no distinct band to disappear from the spectrum of 1 : 2-naphthaquinone 1-oxime, but it is possible that the γ-OH band coincides with the strong one at 857 K, a shoulder on this band being reduced after deuteration.

Some characteristic absorption bands (K) *of quinone monoximes.*

No.	Compound	Peaks near 3000 K, A *	Peaks near 3000 K, B *	ν OD, A
1	1 : 4-Benzoquinone monoxime	3166; 3050; 2835; 2770	3540; 3200; 2845	2300; 2140
2	1 : 4-Naphthaquinone monoxime	3165; 3068; 2927; 2845	3550; 3245; 3050	2292; 2155
3	1 : 2-Naphthaquinone 2-oxime	3210	3555; 3225; 2835	2375
4	1 : 2-Naphthaquinone 1-oxime	2700	2700	2000
5	1 : 2-Naphthaquinone 1-methoxyimine	—	—	—
6	1 : 2-Naphthaquinone 2-methoxyimine	—	—	—

	νC=O								
No.	simple, A	B	deuterated, A	νC=N, A	δOH, A	δOD, A	νN-OX, A (X = H or CH_3)	νN-OH, B	νN-OD, A
1	1628	1648	1632	1555	1450	1092	1037	1025	1030
2	1630	1655	1626	1577	1442	1095 sh	975	968	951
3	1668	1680	1663	1550	1432	1086	1069	1060	1065
4	1618	1632	1616	1526	?	1060 sh	1075	1078	1055
5	1670	—	—	1515 ?	—	—	1058	—	—
6	1660	—	—	1520 ?	—	—	1010	—	—

* A = solid, B = solution in $CHCl_3$ (saturated, 0·3 mm. cell). sh = shoulder.

Region between 2000 *and* 3600 K, *and Hydrogen Bonding.*—The spectra of individual oximes differ considerably in this region. The oximes of benzoquinone and 1 : 4-naphthaquinone in the solid state show strong and broad absorption bands centred around 2900 K, bearing several peaks (Fig. 3). These bands are due to the stretching of bonded OH groups, and some of the subsidiary maxima may arise from combination or overtones reinforced by the interaction with the νOH vibration mode. In solution (saturated in $CHCl_3$, 0·3 mm. cell), this absorption is replaced by two strong and broad bands, and a third, sharp band with a larger wave number. The latter is certainly due to the stretching of free hydroxyl groups. The appearance of two bands due to bonded hydroxyl groups has been mentioned in connection with simple oximes,[14] but no adequate explanation has been offered. The possibility has been mentioned of two types of association, O–H · · · O= and O–H · · · N, respectively. This can be eliminated in our case, because one distinct carbonyl band only can be found in solution, whereas two would be required by the above scheme, one due to bonded carbonyl and the other to free groups. Geometrical isomerism with subsequent differences in the strength of the hydrogen bonding is possible with 1 : 4-naphthaquinone oxime, but not with the benzoquinone oxime. The splitting of the νOH band appears also in the spectra of solid substances, and it may be particularly well observed in deuterium-substituted compounds (Fig. 3*b*; since the spectra of the two compounds discussed are very similar, only one is reproduced). Resonance splitting due to interaction of νOH vibrations in the hydrogen-bonded polymer appears improbable in view of the size of splitting (about 150 K in the deuterated solid). Interactions with lattice vibrations are also improbable, since the extent of the splitting is about the same in both compounds, which differ considerably, however, in size and shape of the molecules. The splitting may be an inherent characteristic of the hydrogen bond, as it seems to be with several other substances, *e.g.*, sulphinic acids, seleninic acids, 3-hydroxytropone, 4-hydroxypyridine oxide, etc.[15]

1 : 2-Naphthaquinone 1-oxime has quite different absorption in this region. Amstutz, Hunsberger, and Chesswick [16] could not detect any νOH band, but in sufficiently thick

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[14] Califano and Lüttke, *Z. phys. Chem.*, 1955, **5**, 240.

[15] Bratož and Hadži, unpublished work.

[16] Amstutz, Hunsberger, and Chessick, *J. Amer. Chem. Soc.*, 1951, **73**, 1220.

layers of the solid, or in concentrated solution in carbon tetrachloride (0·2 mm. cell), a very weak and broad absorption appears, centred at about 2700 K. An analogous band appears in the deuterated compound at about 2000 K. Such broad and weak νOH bands have been met with in compounds where the hydroxyl group is part of a chelate ring, as in enolised diketones,[17] hydroxyquinones,[18] and hydroxyazo-compounds.[19] In the present case chelation explains also the small difference in position of the carbonyl band in the spectrum of the solid substance and its solution.

Although chelation would be possible on steric grounds also in 1 : 2-naphthaquinone 2-oxime, it does not occur as shown by a strong band at 3210 K in the spectrum of the solid compound. For its solid deuterated analogue there is also a single band only at 2375 K, whereas two strong bands appear again with its solution in chloroform. In carbon tetrachloride, however, a very weak and broad absorption centred at about 2800 K is apparent, very similar in shape and intensity to that for 1 : 2-naphthaquinone 1-oxime. This type of absorption indicates that 1 : 2-naphthaquinone 2-oxime also is chelated in carbon tetrachloride in contrast to the intermolecular association in the solid state and in concentrated solution in chloroform. Under the latter conditions, the oxime necessarily has a configuration which is *anti* to the carbonyl group. The observed chelation in carbon tetrachloride indicates either that a transformation occurs to the *syn*-configuration with retention of structure (this might occur without large energy requirements if the nitroso-form is assumed as intermediate), or that the compound is altogether in the nitroso-form. The latter form also permits formation of a strong intramolecular bond O–H ··· O–N. A decision between the alternatives cannot be reached by means of infrared spectroscopy because of the low solubility of the substance in carbon tetrachloride. The absorption of the hydroxyl group could be recorded only by using a 5 cm. cell, and the rest of the spectrum was then obscured by the solvent absorption. An attempt to solve this point by measuring the electronic absorption was thwarted by the low solubility : only a 1 cm. cell could be used with the instrument available and a saturated solution of the 1 : 2-naphthaquinone 2-oxime gave a slight absorption peak at 725 mμ. The extinction was at the limit of sensitivity of the instrument, hence the molar extinction coefficient could be only estimated and was found in several measurements to be of the order 50—100. This band might be indicative of the nitroso-form,[20] particularly because it does not appear in the chloroform solution of the same substance in which the oxime form has been shown to predominate. This result is rather surprising since the isomer, 1 : 2-naphthaquinone 1-oxime, also chelated, exists under all conditions in the oxime form,[2] but support comes from the relative solubilities : 1 : 2-naphthaquinone 1-oxime is readily soluble in carbon tetrachloride, the isomer only very sparingly so.

FIG. 3.

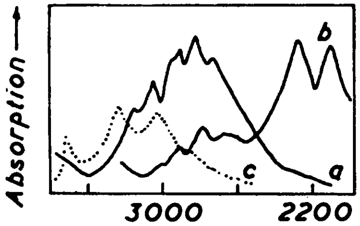

FIG. 4.

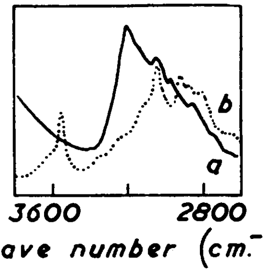

FIG. 5.

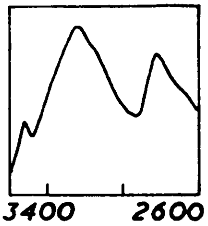

FIG. 3. 1 : 4-*Naphthaquinone monoxime : solid* (*A*), *deuterated solid* (*B*), *oxime dissolved in* $CHCl_3$ (*C*).

FIG. 4. 1 : 2-*Naphthaquinone 2-oxime, solid* (*A*), *dissolved in* CCl_4 (*B*).

FIG. 5. 1 : 2-*Naphthaquinone 2-oxime, dissolved in* $CHCl_3$.

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[17] Rasmussen, Tunnicliff, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068.

[18] Hadži and Sheppard, *Trans. Faraday Soc.*, 1954, **50**, 911.

[19] Hadži, *J.*, 1956, 2143.

[20] Hertel and Lebok, *Z. phys. Chem.*, 1940, **47**, *B*, 315.

Experimental.—The substances were prepared and purified by conventional methods. Deuterated benzoquinone oxime was prepared by recrystallisation from D_2O. No exchange occurred in CH groups since a solid sample of the deuterated material regained the spectrum of the ordinary compound on exposure to the atmosphere for 2 days. Other oximes were deuterated by a technique described previously.[19] The spectra were recorded on a Perkin-Elmer spectrometer model 21 equipped with a rock-salt prism. Paraffin oil and hexachlorobutadiene were used for mulling the solids. The chloroform used as solvent was an analytical reagent, containing about 0·5% of ethanol, and was not further purified. The carbon tetrachloride was refluxed over phosphoric oxide.

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