

CHARACTERISTIC FEATURES IN INFRARED SPECTRA OF 1,3,4-OXADIZOLIN-5-ONES*

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Abstract. It is noted that the high frequency is the main characteristic of 1,3,4-oxadiazolin-5-one. Underlying reason for this and other peculiarities in the IR spectra of 1,3,4-oxadiazolin-5-one are discussed.

The IR spectrum represents transitions between the possible vibrational energy levels of a given molecule. Characteristic absorption bands are obtained for various functions, such as aromatic and aliphatic CH, vinyl, nitriles, azide, isocyanates, and different types of carbonyls, which help in the elucidation of the structure of the molecules.

The carbonyl linkage exhibits strong absorption bands in the region of 1540–2000 cm^{-1} . This is probably the most useful portion of the IR region, because the position of this functional group is quite sensitive to the substituent effects and the geometry of the molecule. This group falls next in line to the hydroxyl group as far as the sensitivity to physical conditions is concerned. Generally the highest recorded frequency is observed in vapour phase,¹ but due to its high polarity it is also affected by the polarity of the solvent. Changes in the bond angle have a marked effect on the absorption of the carbonyl, as is clearly shown by the small ring carbonyl compounds, e.g. cyclopropanones.² As a general rule, constriction of the bond angle increases the frequency.²⁻⁵ Electronegativity, hybridization of the substituent atoms, and hydrogen bonding make substantial contribution to its absorption position.

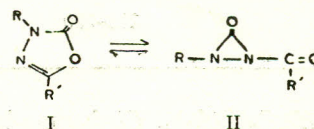
IR spectroscopy among other methods of analyses has proved to be a very useful tool in the elucidation of structure of 1,3,4-oxadiazolin-5-ones and the related compounds. In the IR region the oxadiazole and oxadiazolinone⁶⁻⁸ ring has been characterized^{4,6,7,9-12} by bands in the region of 970 cm^{-1} due to N—N bond, 1020–1330 due to C—C bond, and 1560–1640 due to C=N bond. In the 4-substituted 1,3,4-oxadiazolinones the C—O—C linkage appears as high as 1388.^{4,6,7,9-12} The carbonyl frequency in these compounds appears at unusually high frequency of about 1800 cm^{-1} , or even higher, with shoulder around 1850.^{4,6,10} This is the case even in condensed form. The tautomeric form with the hydroxyl group at position five is ruled out because of the fact that the position of carbonyl absorption is same in parent as well as substituted compounds. The same is true for the 1,3,4-oxadiazolin-5-thiones, in which the presence of C=S absorption bands at 1438–1538 cm^{-1} is compatible with a thione structure.^{5,9,12}

Discussion

From the data presented in Table 1 it follows that

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the oxadiazolinones(I), absorb in the 1780–1825 cm^{-1} region.^{4,6-10} This seems to be a rather high position for a five-membered ring. On this account at first they were assigned a diaziridinone structure(II).^{4,13-16}

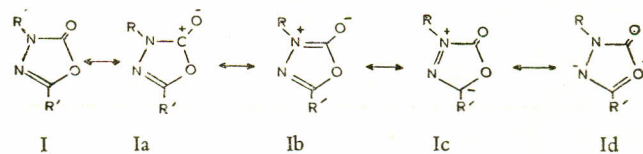


The strained carbonyl^{2,3} absorbs at a higher frequency, e.g. cyclopropanone first synthesised by Turro and Hammond,² absorbs at 1813 cm^{-1} . Green and Stowell³ have reported the carbonyl absorptions at 1880 and 1862 with shoulders at 1926 and 1800 cm^{-1} for the compound III.



As mentioned above electronegativity and hybridization of the substituent atoms on the carbonyl carbon also affect the absorption frequency of a given carbonyl group, which is clearly shown by the examples of cyclopropanone and diaziridinones.³ This is because 2s orbital on a carbon is more electron attracting than 2p orbital.¹⁷ Thus as the amount of the s character increases, the electron attracting ability of carbon approaches that of chlorine, which is evident from resulting reduced dipole moment in the alkyl halide,¹⁸ e.g. cyclopropyl chloride has a dipole moment of 1.76 D versus 2.08 D in cyclopentyl chloride. This indicates greater s character in the external bonds of cyclopropanes.¹⁸

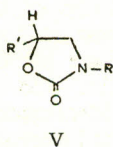
The oxadiazolinone ring I, may be looked at as a combination of lactone and lactam⁷ type of structure, in which the nitrogen atom next to carbonyl becomes very strongly electropositive on account of contribution by the resonance form Ic. The strong electron withdrawing effect of this nitrogen atom might contribute to the increase in the carbonyl frequency of such ring structures. This effect is supported by the oxygen atom of the ring and the cumulative electron



withdrawing effect strongly enhances the carbonyl frequency from the usual position of the five-membered rings.

The carbonyl absorption of the 1,2-diazetidinediones¹⁹ is known to appear above 1800 cm^{-1} . Thus di-*t*-but-1,2-diazetidinedione exhibits the carbonyl band in the IR at 1813 cm^{-1} . This is indicative of a strained amide carbonyl function. One may extend the comparison to diphenyluretidinedione¹⁹ which absorbs at 1775 unfused β -lactams absorb within the range 1730–1760 cm^{-1} .⁵

The high carbonyl frequency seems to be quite characteristic of the 1,3,4-oxadiazolinone ring, since in the case of oxazolidones²⁰ it may be noted that the carbonyl absorption falls in the usual range of a five-membered ring.



Where (a) R, *p*-tolyl; R', Ph; C=O 1733 cm^{-1} . (b) R, *n*-butyl; R', butoxymethylene; C=O 1750 cm^{-1} . and, (c) R, *p*-tolyl; R', phenoxymethylene; C=O 1735 cm^{-1} .

This apparent anomalous behaviour is governed by a number of factors, such as, resonance, strained bond angle, and the presence of a C=N bond in the ring, which apparently constricts the bond angles. The most stable configuration of five-membered ring system is the puckered form which enables the carbon atoms to attain the optimum angle closest to the angle for the sp^3 hybrid carbon atom, and does not impart any extra potential energy to the molecule. Introduction of a C=N bond in the ring causes the atoms to deviate from the optimum bond angle. Consequently the molecule is forced into a configuration wherein the distortion of bond angle results.

Knittle and his coworkers²¹ have reported the carbonyl absorption in certain oxadiazolinones as high as 1835 cm^{-1} . It is suggested that the N=N bond exerts its influence directly at the carbonyl, where sp^2 nitrogen acts inductively, somewhat like a halogen atom and indirectly at the γ -carbon, which transmits an inductive effect to the ether oxygen. An electronegative γ -substituent in γ -lactone is known to raise carbonyl absorption substantially⁵ (chapter 11). This is endorsed by the fact that oxadiazoles and oxadiazolinones exhibit an absorption band in the region of 1510–1560 cm^{-1} which is due to the N=N stretching²¹. This fact also supports the participation of the resonance forms like Ic to the resonance hybrid of the oxadiazolinones. In the case of *p*-anisyl and *p*-nitrophenyl groups^{6,10} the carbonyl frequency is lowered to a certain extent. This certainly is not due to the resonance effects, rather other factors such as steric effects, are operative. But the effect is not very marked. This is also quite understandable, since the carbonyl function is not conjugated with the substituents at position 2 of the oxadiazolinone ring.

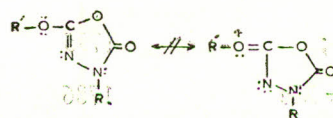
If one observes the C=N absorption frequencies it immediately becomes clear (Table 1) that it is lower

in case of phenyl or other substituents as compared to the alkoxy substituents. The trend of the phenomenon may, however, be noted as the absorption frequency is the lowest in case of *p*-nitrophenyl, and highest in *p*-anisyl, with phenyl occupying intermediate position. This seems to create a definite pattern in connection with the electronegative properties of the substituent groups. In case of alkyl and substituted-alkyl groups it may be noted that the C=N frequency again shoots up as high as 1642 cm^{-1} , near the value for alkoxy substituents, which is perhaps due to electron donating properties by hyperconjugation of such groups.

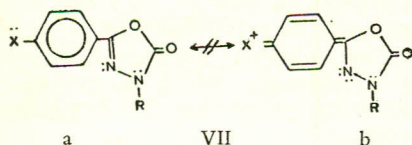
In case of strong electronegative groups such as trifluoromethyl as the substituent, the C=N group frequency¹² in oxadiazoles lies at 1576 cm^{-1} . In case of alkoxy groups the frequency goes up to 1628 in oxadiazoles,^{11,12,22} and 1640–60 cm^{-1} in case of oxadiazolinones.^{4,6,7,11,22} It goes down again to 1570–1578 cm^{-1} when alkoxy groups are replaced by substituents of varying electronegativities^{11,12,22} from CF_3 to CH_3 and *p*-anisyl.⁶

To summarise, the C=N frequency in oxadiazolinones varies as follows: alkoxy, alkyl > *p*-anisyl > phenyl > *p*-nitrophenyl.

From the above discussion it follows that the position of the absorption of the C=O and C=N is a direct consequence of special electronic and resonance effects induced in the ring by the presence of various heteroatoms. One may also consider the plane of the substituent with respect to the plane of the pi -orbitals of the C=N function. It may be that the plane of the substituents on the ring is different (perpendicular or other) from that of the C=N function so that overlap with the pi -orbitals of C=N groups may not be possible, and consequently there is no resonance involved between the C=N and the big aryl substituent on the oxadiazolinone ring. On account of this only the electronegative properties of the various groups have any bearing on its absorption position. This indicates lack of participation of the aryl group. This consequently restricts the 'flow' of electrons to and from the C=N function to various substituents on position two on the ring. This lack of conjugation between the aryl groups and the C=N bond may be the reason why absorption frequency of C=N in case of *p*-anisyl, phenyl and *p*-nitrophenyl does not differ to any significant degree. This also endorses the hypothesis of the phenyl group being perpendicular to the oxadiazolinone ring, and is also in formal agreement with the observation that conjugation with an aryl group lowers the carbonyl absorption frequency to a lesser extent than a C=C bond. The latter phenomenon is obviously due to the fact that the electron 'flow', from the aryl ring to the C=O would not be spontaneous as it would involve a high activation energy



on account of the fact that aromaticity of the aryl group would be 'destroyed'. Further it would involve an extra 'expenditure' of 36 kcal/mole in terms of resonance energy. Keeping this in view it is apparent that the resonance form VIIb would contribute very little to the resonance hybrid, particularly so in cases



of strongly electronegative groups like nitro.

It may be concluded from the above discussion that the resonance effects play less important role in connection with the absorption frequency of the C=N function in the oxadiazolinones. Rather the electronegativity of the atom and its size (mass effects, spatial arrangement of the substituents), play an important role.

Experimental

The oxadiazolinones were obtained in two ways:

1. By the reaction of carbalkoxynitrenes^{4,7,8} obtained by the photolysis of alkylazidoformates in the presence of isocyanates.

2. Independent synthesis following the procedure of Freund²³ and Darnow.²⁴

The reaction mixture was subjected to photolysis in a silica-tube, suspended in the centre of a Raynot photo chemical chamber, which consisted of sixteen tubular UV lamps mounted around the inner surface

of a polished cylindrical-reflector. Low pressure mercury-lamps emitting their maximum at 253 nm were used.

The reaction mixture of azide and the isocyanates was irradiated for 24 hr. Evolution of nitrogen gas was measured by the displacement of water in a burette and from this the amount of the azide decomposed was calculated correcting for the vapour pressure of the isocyanate. The excess isocyanate was removed under reduced pressure and the residue was molecularly distilled using Hickmann still.²⁵ The oxadiazolinones were separated from the crude product mixture by the vapour phase chromatography (VPC) using a 20% Ucon polar (20HB 2000) column of 8 ft × ¼ in and 2 ft × ¼ in dimensions under the following conditions: column temperature, 145°C; detector temperature 180°C and injector temperature 180°C; gas-flow (helium) 60 ml/min. Yield of the oxadiazolinone is 10-15%. The compounds gave satisfactory elemental analyses which were done by M.H.W. Laboratories, Garden City, Michigan, and A. Bernhardt, Max Planck Institut für Kohlenforschung, West Germany. Gas chromatographs used were the Wilkens aerograph model A-90-P3, or the Autoprep model A-700.

For the independent synthesis the following scheme was used:

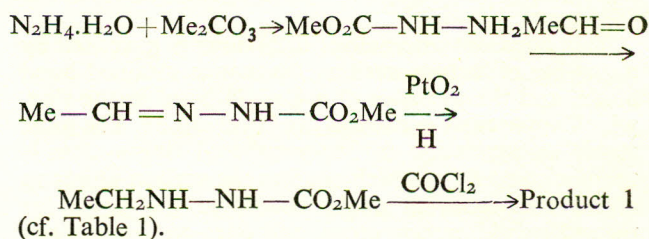


TABLE 1. IR ABSORPTION FREQUENCIES OF REPRESENTATIVE COMPOUNDS FREQUENCY IS GIVEN IN WAVE NUMBER (cm⁻¹).

Compound	C=O	C=N	C—O—C	N—N	Significant bands in fingerprint region
R = Et; R' = OMe	1805	1660	1380	928	1450(s);1305(m);1072(m) ^a
	(sh. at 1850)				962 (m);828(m);792(m).
R = Et; R' = OEt	1805	1640	1384	944	1420(s);1384(s);1357(s); ^a
					1047(s);978(s);896(m).
R = Me; R' = OEt	1805	1640	1380	960	1430(s);1328(s);1350(m); ^a
	(sh. at 1850)				1072(m); 1012(s);900(s).
R = Et; R' = phenyl	1800	1612	1450	930	1598(s);1575(s);1500(m); ^b
	(sh. at 1780 and 1865)				1450(s);1018(s);958(m);
R = Et; R' = <i>p</i> -Anisyl	1780	1615	1255	867.5	930(m); 682(m).
					1510(s);1310(m);1255(s); ^b
R = <i>t</i> -but	1780	1620	1255	940	975(m); 867(s); 777(s).
R' = <i>p</i> -anisyl					1510(s);1465(s);1360(m); ^b
					1315(m);1255(s);1170(s);
					1032(s).
R = Et; R' = <i>p</i> -nitro-phenyl	1775	1600	1230	850	1505(s);1410(m);1350(s); ^b
					1335(s);1230(s);1110(s);
					1060(m);850(s).
R = ph-CH ₂ -;	1795	1642	1314	935	1343(s); 1437(s). ^c
R' = Me					
R = H; R' = Me	1786	1650	1321	935	1390(s); 1435(s). ^c

^a, Ref. 4,6; ^b, ref. 6; ^c, ref. 7

IR spectra were obtained with Perkin-Elmer models 421 or 621 and a Beckman IR 8 spectrophotometer. The spectra were taken in a CCl₄ solution using a Perkin-Elmer micro cell. Some spectra were taken in a KBr disc or as thin films of liquids. The position of absorption bands are reported in the frequency units of wave numbers.

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