Tetrahedron. Vol. 26, pp. 3429 to 3434. Pergamon Press 1970. Printed in Great Britain

A STUDY OF PYRAZOLIN-5-ONE TAUTOMERISM—III

AN INFRARED ABSORPTION BAND SPECIFIC FOR THE OH FORM[1]

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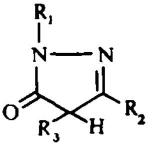
(*Received in the UK* 13 *March* 1970; *accepted for publication* 25 *March* 1970)

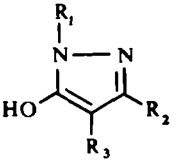
Abstract—Pyrazolin-5-ones, including those having a 3- or 4-substituent, can be identified in the OH tautomeric form by the presence of an IR absorption band found in the region 3175–25 cm^{-1}. This absorption band has been assigned to the CH stretching vibration of an aza-1:3-diene-like configuration in the pyrazolone ring.

INTRODUCTION

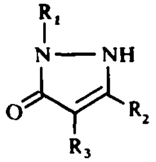
PREVIOUS publications[1,2] have described attempts to distinguish between the tautomeric forms in 1-aryl-2-pyrazolin-5-ones using NMR and IR spectroscopy. The three possible tautomeric forms are:



CH FORM



OH FORM



NH FORM

The first indication of the OH form is the absence of a ring CO absorption but if a mixture of tautomers, or substituents containing CO groups, are present the interpretation becomes much more difficult.

We have observed that a certain IR absorption band is found in the spectra obtained from pyrazolinones known to be in the OH form, and that the converse is also true. This paper deals with the assignment of this vibration and the proof of its specificity to the OH tautomer.

RESULTS

IR absorption spectra

The IR absorption band which forms the subject of this paper is a sharp peak of medium to weak intensity found in the region 3175–25 cm^{-1} (Fig 1). It is most readily observed when the 1-aryl-2-pyrazolin-5-ones are examined in the solid state (Table 1).

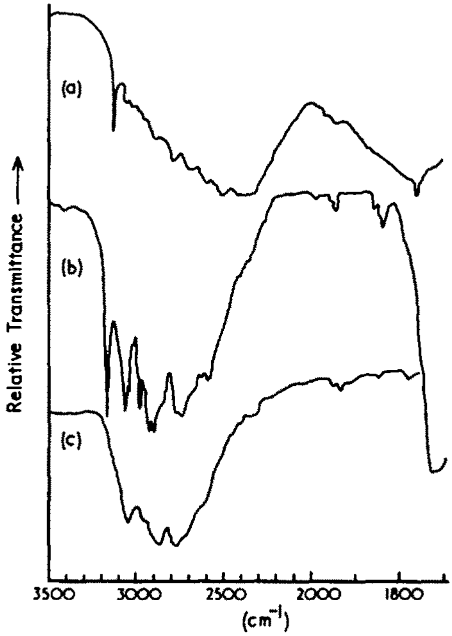


FIG 1. The IR spectra (3500–1800 cm^{-1}) of: (a) 1-phenyl-2-pyrazolin-5-one; (b) 4-ethoxycarbonyl-1-phenyl-2-pyrazolin-5-one; (c) 3,4-dimethyl-1-phenyl-2-pyrazolin-5-one. Examined in the solid state (KBr disc)

In all these examples the OH tautomeric form had been previously established. Although this absorption is observable when the compounds are examined as dispersions in mineral oil, better results are obtained from KBr discs or from dispersions in hexachlorobutadiene. This is because the absorption, although sharp, tends to be

TABLE 1. ABSORPTION FREQUENCIES DISCRETE FOR THE OH TAUTOMER

Compound	*Substituent*			*Frequency* (cm^{-1})	*Intensity*	*Media*
	R_1	R_2	R_3			
1	C_6H_5	H	H	3130	mw, sp	Solid
				3150	w,sh	$CHCl_3$*
2	O—$NO_2C_6H_4$	H	H	3130	mw	Solid
3	C_6H_5	CH_3	H	3130	mw, sp	Solid
4	C_6H_5	$COOC_2H_5$	H	3140	vw, sh	$CHCl_3$*
				3145	w	Solid
5	C_6H_5	H	$COOC_2H_5$	3170	m, sp	Solid
6	O—$NO_2C_6H_4$	H	$COOC_2H_5$	3150	m, sp	Solid

* Mixture OH + other tautomers.[1]
m=medium, w=weak, v=very, sh=shoulder, sp=sharp.

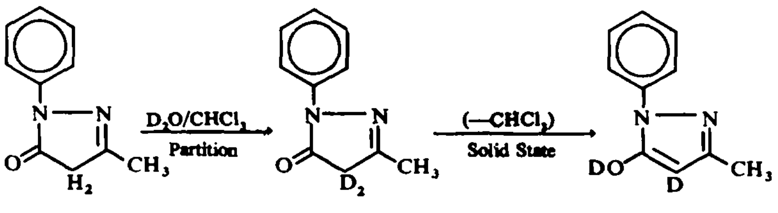
relatively weak in intensity and when a dispersion in nujol is examined it appears as a weak shoulder to the strong CH stretching absorption, owing to the mulling agent. As shown in Table 1, the absorption band is also obtained on examination of solutions in chloroform, where it appears to be extremely weak, although no example was available for comparison where the OH tautomer almost exclusively existed in this solvent.

ASSIGNMENT

It must first be established that this absorption band does not arise from combination or overtone bands. The most likely possibilities are the first overtones of $\nu_{C=C}$ (pyrazolone- or phenyl rings) or $\nu_{C=N}$, all of which are found in the 1620–1500 cm^{-1} region, or combination bands due to permutations of any two of the previously mentioned possibilities. Whereas in some cases numerically correct values for overtone or combination bands are obtained, there was no consistent assignment for all of the compounds. Furthermore, in some examples, e.g. 4-ethoxycarbonyl-1-phenyl-2-pyrazolin-5-one the absorption peak appeared to be too strong for an overtone or combination band. Consideration of the three tautomeric forms suggests that an absorption specific to the OH form must either be associated with the OH group or with the azadiene-like $(\text{—}C{=}\overset{H}{C}\text{—}\overset{H}{C}{=}N\text{—})$ configuration of the pyrazolinone ring.

Because of intermolecular H-bonding, the OH absorptions in the solid state spectra appear as very broad multiplets and it is possible that the sharp peaks found near 3150 cm^{-1} could have been related to the OH hydrogen bonding. However, the fact that absorptions due to the phenyl ring CH stretching vibrations are clearly visible in the region 3100–3000 cm^{-1} seems to eliminate the possibility that the 3175–25 cm^{-1} peak is a shoulder of the OH absorption, because it would be expected that these absorptions would be hidden by the large absorption band. We thus deduced that the assignment was most likely due to the azadiene-like configuration, for which a CH stretching vibration would be expected in approximately this spectral region. This assumption is supported by the fact that the IR spectrum of 3,4-dimethyl-1-phenyl-2-pyrazolin-5-one, which is known to exist in the OH form in the solid state,[3] did not contain such an absorption (Fig 1).

All other confirmatory experiments were carried out on 3-methyl-1-phenyl-2-pyrazolin-5-one, compound 3, which has an absorption band at 3130 cm^{-1}. The IR spectrum of this compound (Fig 2a) has been widely studied in the solid state but no assignment of the absorption at 3130 cm^{-1} has previously been given.[3-8] From previous NMR studies it was known that by shaking a deuterochloroform solution of compound 3 with D_2O rapid exchange of both protons on the 4-position was obtained. An NMR examination of the chloroform solution confirms that there is no resonance or coupling from any 4-H's. For IR spectroscopy this experiment was repeated with chloroform as the solvent. After deuteration, the solvent was evaporated off and the



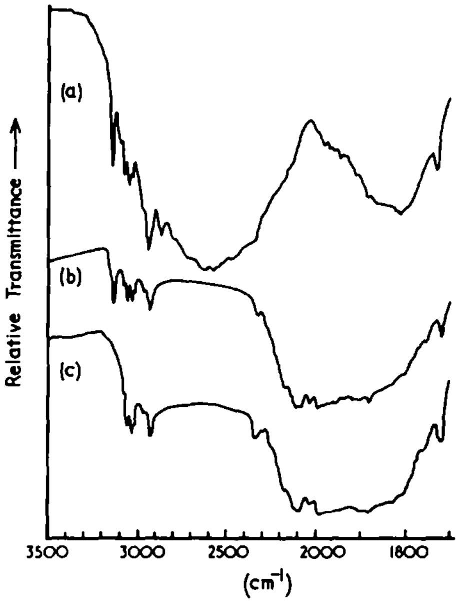
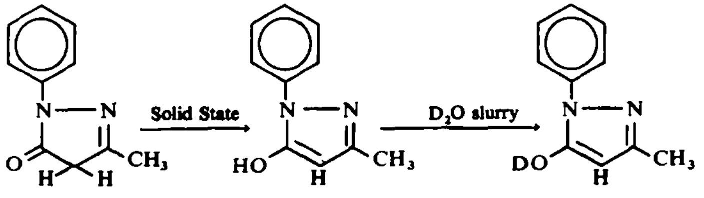


FIG 2. The IR spectra (3500–1800 cm^{-1}) of: (a) 3-methyl-1-phenyl-2-pyrazolin-5-one; (b) 3-methyl-4-monodeutero-1-phenyl-2-pyrazolin-5-one; (c) 3-methyl-4-dideutero-1-phenyl-2-pyrazolin-5-one. Examined in the solid state (KBr disc)

IR spectrum of the solid was examined (Fig 2c). As expected, the broad OH absorption had been replaced by a broad OD absorption found at lower frequencies and the 3130 cm^{-1} band disappeared. This confirmed that the absorption was due either to OH or CH bonds and that it did not arise from overtone or combination bands. The molecular weight of the deuterated compound $C_{10}H_8D_2N_2O$ (176) was confirmed by means of mass spectrometry, using accurate mass measurement on the parent peak (Found: 176·090590, Calc. 176·091864).

A sample of compound 3 was then shaken up with D_2O so that the D atoms were exchanged with H atoms in the solid. In this experiment the solid compound is fixed in the OH/NH state and exchange occurs slowly (6 weeks). The D_2O was filtered and the solid was dried before its IR spectrum was examined. The result (Fig 2b) indicated that the H atom of the OH group only had exchanged with D_2O. The 3130 cm^{-1} band was still present whereas the broad OH absorption had been replaced by a broad OD absorption found at lower frequencies, identical with Fig 2c, thus confirming the assignment. The mass spectrum contained a molecular ion at 175 ($C_{10}H_9DN_2O$). The



use of accurate mass measurement confirmed the molecular formula (Found: 175·085445, Calc. 175·085587) and the possible presence of any di-deutero compound was eliminated.

It is possible to recrystallize compound **3** from boiling D_2O. In this case the principal product obtained was 3-methyl-4-dideutero-1-phenyl-2-pyrazolin-5-one. It was not possible to detect any monodeutero compound in the mass spectrum because its parent ion would be coincidental with the ion formed by loss of a proton from the dideutero compound.

Thus heating compound **3** in D_2O apparently disturbs the tautomeric equilibrium and deuteration then proceeds through the CH tautomer.

The presence of an IR absorption band in the 3175–25 cm^{-1} region of the spectra of other reported pyrazolinones[5] may be observed, for which the same assignment is possible.

DISCUSSION

The absorption frequencies of this C—H stretching vibration obtained from compounds **1–6** are rather high compared with those usually found for the CH vibrations of other alkene groups. The values obtained lie between those found for alkene groups (3080 cm^{-1}) and alkyne groups (3300 cm^{-1}). That the OH tautomer exhibits this IR absorption whereas the other tautomers do not is undoubtedly due to the presence of ring conjugation. It thus seems likely that the 5-hydroxy-1-aryl-pyrazole ring has some aromatic character and that some positions in the ring have a high electron density. Pyrrole, a known π-excessive N-heterocycle,[9] has a CH stretching vibration which absorbs at 3120 cm^{-1}. Other heterocyclic molecules having a CH stretching vibration in this region are pyrazole,[11] furan,[12] and thiophene.[12]

This characteristic CH absorption band is expected to be found in the spectra of the OH tautomer of all 1-substituted pyrazolin-5-ones which have only one further substituent in the 3- or 4-positions. Those compounds which do not have a 1-substituent (i.e. R=H) or those containing substituents whose absorption frequencies mask the alkene CH absorption, e.g. —COOH, $—NH_2$, $—NHCOC_2H_5$, are more difficult. In this case the use of discrete deuteration such as that described in this paper could be extremely useful.

The assignment may also prove useful in many other heterocyclic systems, which have a $—\overset{H}{C}=\overset{H}{C}—\overset{H}{C}=N—$ configuration.

EXPERIMENTAL

The preparation of the compounds has been described previously. Deuteration of the compounds was carried out in a glove box using P_2O_5 as desiccant, with 99·5% D_2O (Merck & Co.) and details of the techniques are described in the text. Spectra were obtained from dispersions in HCB (hexachlorobutadiene) and as KBr discs, examined in a Perkin-Elmer 225 spectrophotometer. Mass spectral measurements were made with an AEI MS-902 instrument.

Acknowledgement—We thank Mr I. Degen for assistance with mass spectral data. We are greatly indebted to Professor A. R. Katritzky for the gift of 3,4 dimethyl-1-phenyl-2-pyrazolin-5-one.

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