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Infrared Analysis of 2-Pyrazolin-5-one Derivatives*

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The ir spectra in the region 4000–250 cm^{-1} in the solid state have been recorded for seventy-six 1,3-di-substituted 2-pyrazolin-5-ones in which 4-positions are coupled with various diazotized anilines. Correlations between structure and frequency are made. From the results obtained, a useful application of these spectral correlations can be derived for recognizing a pyrazolinone dye in an unknown compound by means of its spectrum. The strong bands at about 1650, 1550, 1340, 1260, and 1150 cm^{-1}, and sometimes the strong or medium bands near 1000 and 680 cm^{-1} constitute a good indication of the presence of a 4-arylhydrazono pyrazolinone ring.

INTRODUCTION

Numerous *N*-heterocyclic compounds have been studied by means of ir spectroscopy; however, relatively little is known of the vibrational spectra of 2-pyrazolin-5-one derivatives,[1,2] and only two group vibrations, cyclic C=O and ring C=N, are made. Snavely, Trahanovsky, and Suydam[3] have, however, investigated the spectra of 1-phenyl-3-methyl-2-pyrazolin-5-one in which the 4-position on the pyrazolinone ring is coupled with diazotized aniline, and they have assigned two characteristic frequencies to the corresponding cyclic C=O and N=N group vibrations on the basis of the azo-keto structure.

In the present investigation, systematic studies of the ir spectra of a number of 1,3-diphenyl-, 1-phenyl-3-methyl-, and 1-aryl-3-ethoxycarbonyl-2-pyrazolin-5-one dyes are described in order to obtain information for an inclusive study of the spectroscopic behavior of these dyes. The results obtained may also be of importance with reference to the ir analysis of the 2-pyrazolin-5-one dyes of more complicated structures. The definite structure of the 2-pyrazolin-5-one dyes concerned has recently been established[4] to be the tautomeric hydrazone-keto structure stabilized by chelation corresponding to that assigned by Jones, Ryan, Sternhell, and Wright,[5] and not 4H or 2H azo-keto forms, or an azo-enol form in the solid state and in solutions.

I. EXPERIMENTAL METHODS

A. Materials

The 3-ethoxycarbonyl derivatives used in this study were prepared in connection with another investigation.[6] Two series of 3-methyl and 3-phenyl derivatives were obtained by the coupling reaction of 1-phenyl-3-methyl- and 1,3-diphenyl-2-pyrazolin-5-ones with diazotized anilines.

Diazotization—Method A. The aniline (0.0006 mole) was dissolved in diluted hydrochloric acid (1 ml in 5 ml water) and diazotized with sodium nitrite solution (0.06 g in 2 ml water) below 5°C with hand stirring.

Method B. The aniline (0.0006 mole) was dissolved in hot acetic acid (5 ml) containing concentrated hydrochloric acid (1 ml). On cooling, sodium nitrite (0.06 g) was added to this acidic solution in small proportion below 5°C.

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*This work was performed at the Institute of Physical and Chemical Research, Tokyo.

Coupling Reaction—The resulting diazotized aniline was poured into a mixture of an appropriate 2-pyrazolin-5-one (0.0006 mole) and crystalline sodium acetate (2.5 g) in water (30 ml) using mechanical stirring at room temperature. The colored product which separated was collected and washed with methanol–water. All compounds were recrystallized from the appropriate solvents to constant melting points. All melting points were uncorrected. New compounds were confirmed by the chemical analyses.

B. Spectroscopy

The ir spectra for the region 4000–250 cm^{-1} were recorded employing Perkin–Elmer model 521 granting spectrophotometer with a calibration spectrum of polystyrene film (bands at 1601 and 907 cm^{-1}) superimposed on each chart. Wavelengths are believed accurate to ± 2 cm^{-1} throughout the region between 4000 and 250 cm^{-1}. The samples were measured by the potassium bromide pellet technique.

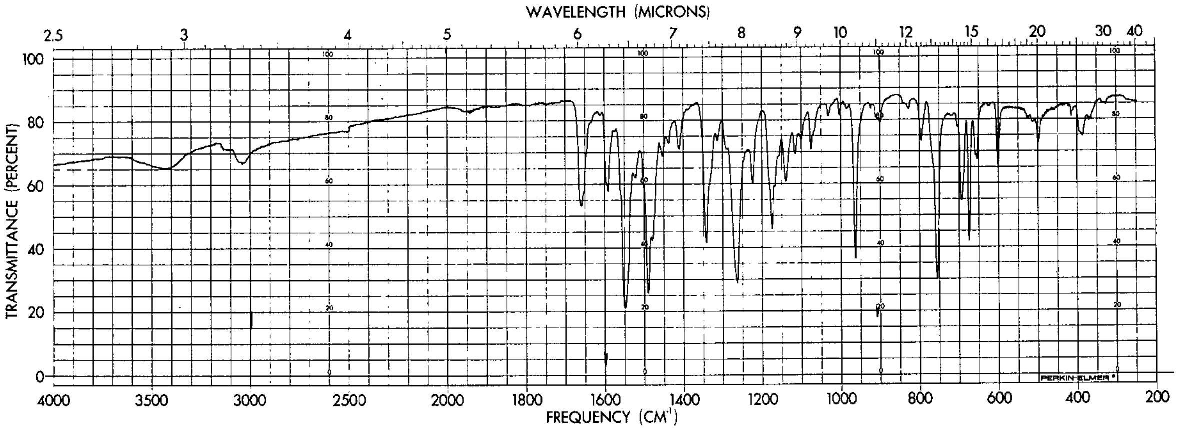


FIG. 1. The spectrum of 1,3-diphenyl-4-phenylhydrazono-2-pyrazolin-5-one (I) listed in Table I.

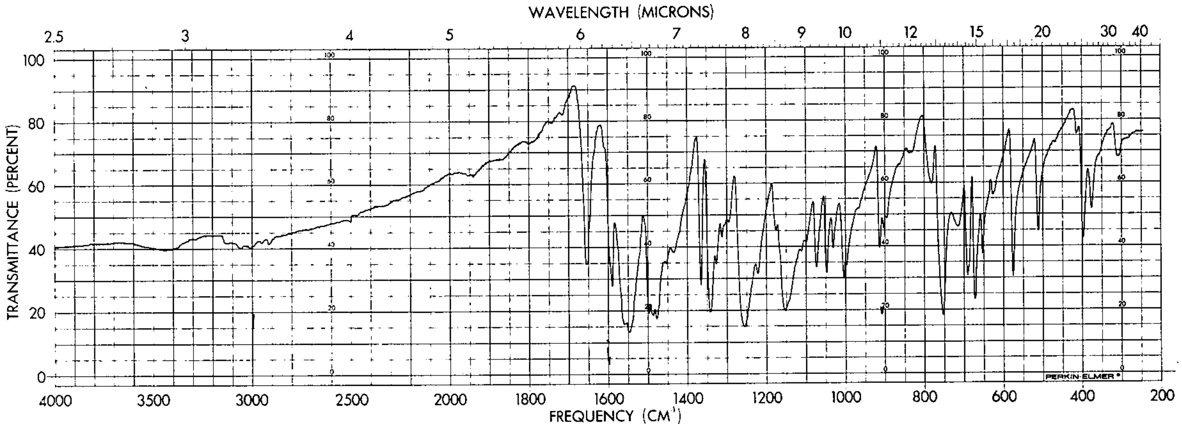


FIG. 2. The spectrum of 1-phenyl-3-methyl-4-phenylhydrazono-2-pyrazolin-5-one (XXXII) listed in Table II.

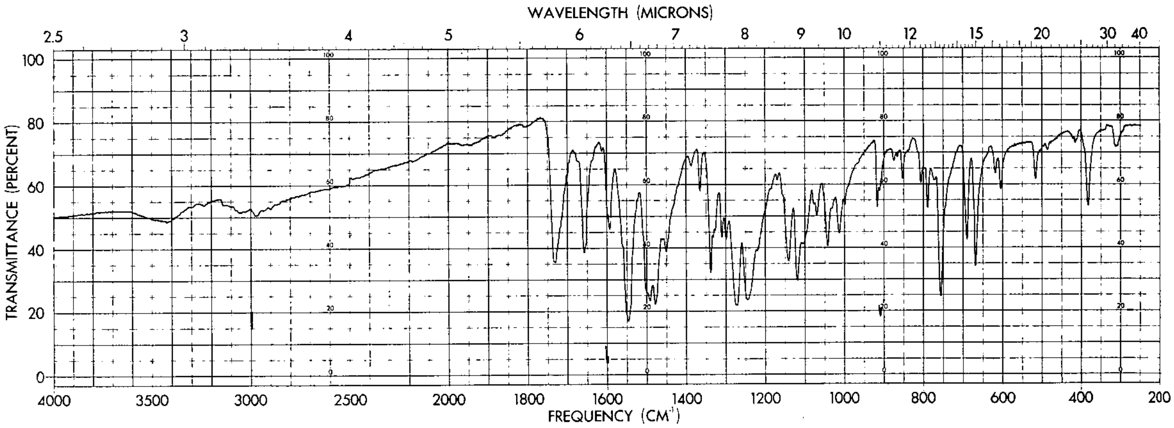


FIG. 3. The spectrum of 1-phenyl-3-ethoxycarbonyl-4-phenylhydrazono-2-pyrazolin-5-one (LVIII) listed in Table III.

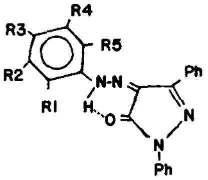
The compounds investigated are listed in Tables I, II, and III. Figures 1, 2, and 3 are typical spectra from each of the three types of compounds, 1,3-diphenyl-4-phenylhydrazono-2-pyrazolin-5-one(I), 1-phenyl-3-methyl-4-phenylhydrazono-2-pyrazolin-5-one (XXXII), and 1-phenyl-3-ethoxycarbonyl-4-phenylhydrazono-2-pyrazolin-5-one(LVIII), described in Tables I, II, and III.

II. RESULTS AND DISCUSSION

The 2-pyrazolin-5-one dyes studied show very weak absorption bands in the region between 4000 and 1800 cm^{-1} when determined in the solid state, but the absorption bands below 1800 cm^{-1} are well represented. The higher frequencies, those over 1800 cm^{-1}, are of little interest for correlative purposes. The spectra of all the compounds examined show very complicated patterns, but a careful investigation can make possible a tentative assignment of almost all the absorptions. The observed frequencies and their tentative assignments are summarized in Table IV.

The cyclic C=O stretching vibration shifts to higher frequency upon an increase in the value of Hammett's σ constant.[7] Thus, electron-donating substituents directly attached to para- or meta-position of the phenylhydrazono moiety cause a shift to a lower frequency; on the contrary, electron-attracting substituents bring about a higher frequency shift. These shifts may be directly attributed to the change of the electron density at the carbonyl group caused

Table I. Physical properties of 1,3-diphenyl-4-arylhydrazono-2-pyrazolin-5-ones.



Compound	R_1	R_2	R_3	R_4	R_5	m.p. °C.	Lit. m.p. °C.[a]	Recrystalilzed from	Appearance[b]
I	H	H	H	H	H	170–1	171	dil. AcOH	YON
II	Me	H	H	H	H	176–7	183	dil. pyridine	RON
III	OMe	H	H	H	H	199–200	209	dil. pyridine	RON
IV	OEt	H	H	H	H	196–7	206	pyridine-MeOH	RON
V	Cl	H	H	H	H	170–1	177	dil. AcOH	YBN
VI	COOMe	H	H	H	H	176–7		dil. dioxane	ON
VII	NO_2	H	H	H	H	194–5	204	dil. pyridine	DBN
VIII	H	Me	H	H	H	168–9	179	dil. pyridine	RN
IX	H	OH	H	H	H	210–11		AcOH	RBN
X	H	OMe	H	H	H	139–40		dil. pyridine	RN
XI	H	Cl	H	H	H	186–7		dil. AcOH	YON
XII	H	Br	H	H	H	171–2		dil. dioxane	ON
XIII	H	COOEt	H	H	H	172–3		dil. dioxane	RON
XIV	H	H	Me	H	H	185–6	193	dil. pyridine	RON
XV	H	H	OH	H	H	228–9		AcOH	BON
XVI	H	H	OMe	H	H	160–1	167	dil. pyridine	RON
XVII	H	H	Cl	H	H	205–6	216	AcOH	RBN
XVIII	H	H	COOBu-*n*	H	H	164–5		dil. dioxane	YON
XIX	H	H	NO_2	H	H	232–3	245	pyridine–EtOH	DRN
XX	Me	Me	H	H	H	197–8		dil. dioxane	RN
XXI	Me	NO_2	H	H	H	229–30		dil. pyridine	RBN
XXII	Me	H	Me	H	H	196–7		dil. dioxane	YON
XXIII	Me	H	NO_2	H	H	274–5		pyridine–MeOH	BYN
XXIV	Cl	H	Cl	H	H	219–20		pyridine–MeOH	DRN
XXV	Cl	H	NO_2	H	H	258–9		pyridine–MeOH	BC
XXVI	I	H	NO_2	H	H	255–6		pyridine–MeOH	RBC
XXVII	Me	H	H	Me	H	203–4		dil. dioxane	RON
XXVIII	OMe	H	H	OMe	H	192–3		dil. dioxane	DBN
XXIX	Me	H	H	H	NO_2	157–8		dil. pyridine	DN
XXX	Me	H	H	H	Me	175–6		dil. dioxane	YON
XXXI	OMe	H	H	H	OMe	158–9		dil. dioxane	YON

[a] D. D. M. Casoni, Boll. Sci. Faci. chim. Ind. Bologna, 9, 4 (1951).
[b] B, brown; O, orange; R, red; Y, yellow; C, crystals; D, deep; N, needles, P, plates.

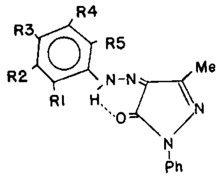
by a combination of resonance and inductive effects produced by the substituents.[8] The cyclic C=O frequencies of the 1,3-diphenyl derivatives, for example, indicate an approximate linear relationship with the constant, corresponding to that described to the 3-methyl derivatives by Toda.[9] This is graphically illustrated in Fig. 4.

The prominent band occurs between 1562–1541 cm^{-1}; this band can be correlated with the peak occurring at 1550 cm^{-1} in the spectrum examined. It is hardly affected at all by a change in the mass, and it can be readily recognized by its consistent sharpness. The band observed can, on the basis of previous results,[4] reasonably be assigned to the benzene ring C=C skeletal vibration associated with the –NH–N= linkage in the 4-position on the pyrazolinone ring.

On the other hand, the band around 1500 cm^{-1} is, in general, fairly intense because of the conjugation between the benzene and the pyrazolinone rings. It is mass-insensitive; accordingly, it is difficult to assign this band to a pure aromatic skeletal mode. The band with no change in its frequency or intensity at about 1500 cm^{-1} may, therefore, be assigned to one of the pyrazolinone ring-stretching vibrations associated with the aromatic C=C skeletal vibration. This band can readily be differentiated from alkane CH deformation frequencies.

In the region 1670–1600 cm^{-1}, an exo-type C=N stretching mode in the 4-position on the pyrazolinone ring is also expected. In the ir region the identification of the carbon–nitrogen double bond is often uncertain, but it appears at 1672–1637 cm^{-1} for the phenylhydrazones.[10] Randall, Fowler, Fuson, and Dangl[1] assigned the band at 1621 cm^{-1} to the ring C=N stretching mode in 1-phenyl-3-methyl-2-pyrazolin-5-ones; Gagnon, Boivin, McDonard, and Yaffe[2]

Table II. Physical properties of 1-phenyl-3-methyl-4-arylhydrazono-2-pyrazolin-5-ones.



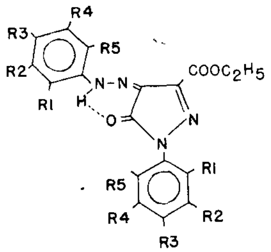
Compound	R_1	R_2	R_3	R_4	R_5	m.p. °C.	Lit. m.p. °C.	Recrystalized from	Appearance[e]
XXXII	H	H	H	H	H	157–8	156[a]	dil. AcOH	YON
XXXIII	Me	H	H	H	H	183–4	185[b]	dil. dioxane	BON
XXXIV	Cl	H	H	H	H	186–7	193[c]	dil. AcOH	ON
XXXV	OMe	H	H	H	H	164–5	166-7[c]	dil. AcOH	YON
XXXVI	OEt	H	H	H	H	145–6	150[a]	dil. AcOH	RBN
XXXVII	H	Me	H	H	H	120–1	120[c]	dil. AcOH	YON
XXXVIII	H	OMe	H	H	H	124–5		dil. dioxane	BON
XXXIX	H	Cl	H	H	H	142–3	144[c]	dil. AcOH	YON
XL	H	Br	H	H	H	156–7	157–8[c]	dil. AcOH	YON
XLI	H	COOEt	H	H	H	130–1		dil. AcOH	YON
XLII	H	OH	H	H	H	210–1		dil. AcOH	YBN
XLIII	H	H	Me	H	H	138–9	139–40[a]	dil. AcOH	ON
XLIV	H	H	NO_2	H	H	197–8	199[a]	dil. dioxane	RN
XLV	H	H	OMe	H	H	138–9	130–40[a]	dil. AcOH	YBN
XLVI	H	H	Cl	H	H	143–4	141–2[c]	dil. AcOH	YON
XLVII	H	H	OH	H	H	213–4		dil. AcOH	DBN
XLVIII	Me	Me	H	H	H	159–60		dil. dioxane	YON
XLIX	Me	NO_2	H	H	H	236–7		dioxane	OC
L	Me	H	Me	H	H	164–5	159[d]	dil. AcOH	RN
LI	Me	H	NO_2	H	H	185–6		dil. AcOH	RBN
LII	Cl	H	NO_2	H	H	232–3		dil. dioxane	YON
LIII	Me	H	H	Me	H	214–5	131[d]	dil. AcOH	BN
LIV	OMe	H	H	OMe	H	162–3		dil. dioxane	BRN
LV	Me	H	H	H	NO_2	188–9		pyridine	DRN
LVI	Me	H	H	H	Me	166–7		dil. dioxane	ON
LVII	OMe	H	H	H	OMe	113–4		dil. dioxane	YON

[a] See Table I, footnote a.
[b] G. B. Cripper and M. Long, Gazz. Chim. Ital. **61**, 99 (1931).
[c] F. A. Snavely and B. D. Krecker, J. Am. Chem. Soc. **81**, 4199 (1959).
[d] G. B. Cripper, M. Long, and G. Perroncito, Gazz. Chim. Ital. **62**, 944 (1932).
[e] See Table I, footnote b.

also gave an assignment for the ring C=N vibration near 1600 cm^{-1} in 4-alkylated 1,3-disubstituted 2-pyrazolin-5-ones. The 1600 cm^{-1} band obtained in previous measurement was supplemented by more recently published ir spectra of the 1-phenyl-3-methyl-2-pyrazolin-5-one dyes.[3] It is not possible to assign the band in this region to a ring C=N vibration if it is one of the pyrazolinone ring-stretching vibrations, and the first benzene ring skeletal vibration should also appear near 1600 cm^{-1}. In all the pyrazolinone dyes investigated, a shoulder band near 1650 cm^{-1}, which appears on the low-frequency side of the cyclic C=O absorption, is often observed. It does not shift when the mass of the substituent is changed. This shoulder could be assigned to an exo type C=N stretching mode of the —NH—N= linkage.

The carbon–nitrogen single bond does not differ much in position from the C—C stretching bands, but it is very intense because of the great polarity of the C—N linkage. The pyrazolinones investigated possess tertiary and secondary aromatic amines in the 1-position on the pyrazolinone ring and in the hydrazono moiety; therefore, the stretching vibration of the $C_{\text{arom.}}$—N linkage should appear in their spectra. Colthup's table[11] shows that the tertiary aromatic amines have strong bands in the 1360–1310 cm^{-1} region. The spectra of the compounds measured show a fairly constant band around 1340 cm^{-1} which may be ascribed to a tertiary aromatic C—N stretching vibration; this frequency is very characteristic of a pyrazolinone ring, and it is hardly affected at all by either changes in the masses or the position of the substituent in the benzene ring. It is not justifiable, therefore, to apply unconditionally the band at 1340 cm^{-1} to the pure tertiary C—N stretching mode. 3-Phenyl-5-chloropyrazole, which has no aromatic tertiary C—N bond, reveals a distinct band at 1370 cm^{-1} corresponding to one of the hetero-ring-stretching modes. The corresponding band is also found at about 1370 cm^{-1} in the spectra of 1,3-diphenyl-5-chloro-4-arylazopyrazoles (LXXVII) having aromatic tertiary C—N bond, however, no other bands could be detected within 1390–1310 cm^{-1} with exception of the 1370-cm^{-1} band. This band may, therefore, be assigned to the coupled vibration

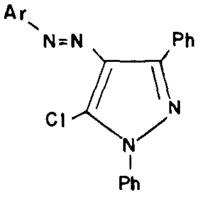
Table III. Physical properties of 1-aryl-3-ethoxycarbonyl-4-arylhydrazono-2-pyrazolin-5-ones.



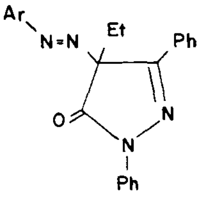
Compound	R_1	R_2	R_3	R_4	R_5	m.p. °C	Recrystalized from	Appearance[c]
LVIII	H	H	H	H	H	151–2[a]	EtOH	YN
LIX	Me	H	H	H	H	112–3[a]	EtOH	YON
LX	Cl	H	H	H	H	179–80[b]	dil. MeOH	YON
LXI	OMe	H	H	H	H	180–1[b]	dil. AcOH	ON
LXII	OEt	H	H	H	H	152–3[b]	dil. AcOH	DON
LXIII	H	Me	H	H	H	141–2[a]	EtOH	YBN
LXIV	H	Cl	H	H	H	157–8[b]	MeOH	YBN
LXV	H	Br	H	H	H	166–7[a]	dil. dioxane	YBN
LXVI	H	OMe	H	H	H	124–5[a]	dil. dioxane	BON
LXVII	H	COOEt	H	H	H	136–7[b]	dil. AcOH	YP
LXVIII	H	H	Me	H	H	142–3[a]	EtOH	YON
LXIX	H	H	Cl	H	H	187–8[b]	MeOH	YON
LXX	H	H	OMe	H	H	163–4[a]	dil. dioxane	YON
LXXI	Me	Me	H	H	H	163–4[a]	dil. dioxane	YBN
LXXII	Me	H	Me	H	H	158–9[a]	dil. acetone	YON
LXXIII	Cl	H	Cl	H	H	210–11[b]	dil. pyridine	DYN
LXXIV	Me	H	H	Me	H	137–8[a]	dil. acetone	BON
LXXV	OMe	H	H	OMe	H	138–9[a]	dil. acetone	DBN
LXXVI	Me	H	H	H	Me	130–1[a]	dil. dioxane	BON

[a] See Ref. 6.
[b] H. Yasuda, Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 56, 267 (1962).
[c] See Table I, footnote b.

of the hetero-ring-stretching and the aromatic tertiary C—N stretching modes. In the cases of 1,3-diphenyl-4-ethyl-4-arylazo-2-pyrazolin-5-ones (LXXVIII), this band shifts to lower frequencies in comparison with those of the compounds, LXXVII, and it appears at about 1340 cm^{-1}. This difference in frequency is probably attributable to dissimilar structures, pyrazole–pyrazolinone rings. On the available evidence the band at 1340 cm^{-1} observed in the pyrazolinon dyes concerned, is tentatively assigned to the ring-stretching mode associated with the aromatic tertiary C—N stretching mode. A strongly absorbing symmetric NO_2 group vibration of a nitro-substituted compound also appears in this region, but a clear distinction between these vibrations is possible. In the typical 3-phenyl derivative I, on the other hand, a well-defined band at 1262 cm^{-1} clearly belongs to the secondary aromatic C—N vibration[12] in the hydrazono moiety, because the band is missing or very weak for the compounds, LXXVII and LXXVIII, and 4-unsubstituted pyrazolinones, which have no secondary aromatic C–N linkage. This C–N vibration is exceptionally sharp in the spectrum, free from other absorption, but it shifts upon a change in the mass of the substituent.



LXXVII



LXXVIII

A band at about 1160 cm^{-1} is very characteristic; its intensity does not change for various compounds of the same series, and it is slightly mass-sensitive in position. This band, however, cannot be related to hetero-ring-stretching modes, because the ring-stretching does not usually occur as low as 1170 cm^{-1}. Furthermore, this band cannot be assigned to a CH in-plane deformation mode caused by benzene ring directly attached to the 1- and/or 3-position on the pyrazolinone ring, both because of the high intensity of absorption over the compounds studied and because of the success in finding it in the 3-methyl- and 3-ethoxycarbonyl-2-pyrazolin-5-ones with no phenyl group. This observation suggests that the observed band can be correlated with the hetero-ring-deformation vibration or the coupled vibration

Table IV. Observed frequencies and tentative assignments in the 1800–300 cm^{-1} region for the 2-pyrazolin-5-one dyes investigated.

3-Phenyl derivatives		3-Methyl derivatives		3-Ethoxycarbonyl derivatives		
$\nu_{av.}$ (cm^{-1})	Intensity	$\nu_{av.}$ (cm^{-1})	Intensity	$\nu_{av.}$ (cm^{-1})	Intensity	Tentative assignment
				1729 ± 7	vs–s	Ester C=O stretching (directly attached to pyrazolinone ring)
1658 ± 22	vs–m	1653 ± 15	s–m	1664 ± 14	vs–s	Cyclic C=O stretching
1642 ± 11	sh	1638 ± 18	sh	1645 ± 10	sh	C=N stretching (exo)
1550 ± 8	vs–m	1552 ± 12	vs–m	1553 ± 7	vs–s	–C=C–NH–N = group vibration
1497 ± 11	vs–m	1495 ± 15	vs–m	1500 ± 15	s–m	C = C skeletal, hetero ring-stretching
		1460 ± 20	m–sh	1450 ± 10	m–sh	CH_3 asym. deformation (methyl and ethoxycarbonyl groups in the 3-position)
				1380 ± 7	m–sh	CH_3 sym. deformation (ethoxycarbonyl group in the 3-position)
		1371 ± 7	m			CH_3 sym. deformation (methyl group in the 3-position)
1340 ± 6	s–m	1340 ± 10	s–m	1331 ± 11	s–m	Tertiary C–N stretching, hetero ring-stretching
1269 ± 19	vs–s	1263 ± 27	vs–s	1290 ± 20	s–m	Secondary C–N stretching
				1253 ± 27	s–m	Ester C–O asym. stretching (directly attached to pyrazolinone ring)
1177 ± 17	vs–s	1168 ± 15	vs–s	1150 ± 15	s–m	Coupled vibration of C–C and C–N stretching
				1112 ± 12	s–m	Ester C–O asym. stretching (directly attached pyrazolinone ring)
		1049 ± 9 1032 ± 6	m m			CH_3 rocking CH_3 rocking (methyl group in the 3-position)
963 ± 5	vs–s	1100 ± 10	s–m	1035 ± 15	s–m	Hetero ring-breathing
671 ± 4	s–m	672 ± 6	s–m	671 ± 5	m	Hetero ring-deformation
610 ± 14	m	598 ± 28	m	609 ± 15	m	Hetero ring-deformation?
498 ± 4	m	515 ± 5	m			Hetero ring-deformation?
401 ± 19	m	392 ± 10	s–m	381 ± 5	m	Hetero ring-deformation?

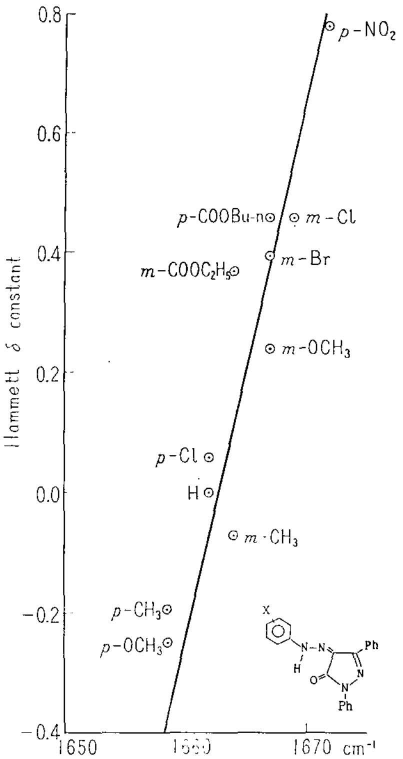


FIG. 4. Correlation between cyclic C=O frequency and Hammett constant of substituent (*X*) on the hydrazono moiety, in 1,3-diphenyl-4-phenylhydrazono-2-pyrazolin-5-one.

of the C−N and C−C linkages, but it is more likely to be the latter vibration from earlier investigation into the five-membered hetero-nucleus.[13-16]

The ring-breathing modes are somewhat difficult to assign, but analogy with the spectra of other hetero-compounds[13-18] indicates that these are to be expected at frequencies below 1100 cm.$^{-1}$ In the frequency range from 1050 to 950 cm^{-1}, strong or medium intensity bands, free from the other bands, are observed in all the spectra examined. The position and intensity are relatively independent of the nature of the substituents of the hydrazono moiety in the same series, but they are considerably altered by the substituents in the 3-position on the pyrazolinone ring. The band in this region is very characteristic, and it can be tentatively assigned to the ring-breathing mode. The ring-deformation modes are also expected at a lower frequency region. A characteristic band with strong or medium intensity is usually detected at about 670 cm^{-1}. This band is mass-insensitive, and has a constant frequency and a similar intensity in the same series. It is more possible, therefore, to assign the band at 670 cm^{-1} to the ring-deformation mode rather than that for some fundamental modes of the other groups.

The correlation of two bands at about 600 and 400 cm^{-1} observed in all the spectra examined is still uncertain, but it may be a characteristic absorption for a pyrazolione ring. The absorptions attributable to the substituents and the aromatics can be readily detected; they can be made with reference to the corresponding spectral region in the assignments based upon the literature. (See Table IV.)

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