CHARACTERISTIC FREQUENCIES IN THE INFRARED SPECTRA OF PYRAZOLINES

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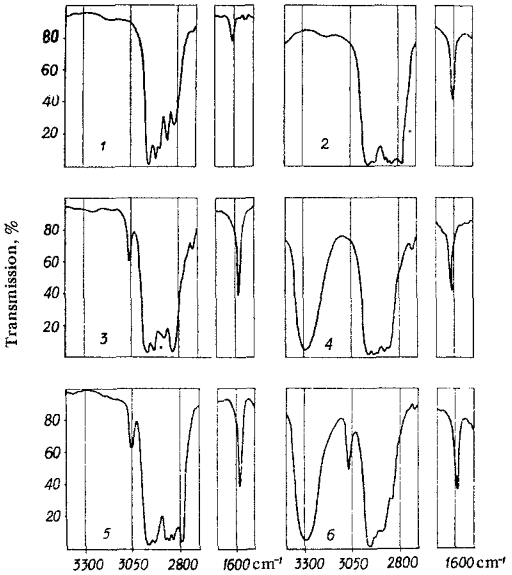
Pyrazolines are characterized by valence vibrations at the following frequencies: C=N (1580–1627 cm^{-1}), $H-C^3=N$ (3040–3063 cm^{-1}), H–N (3270–3305 cm^{-1}) and CH_3-N (2780–2805 cm^{-1}). Lowering of the frequencies of the valence vibrations of C=N in pyrazolines, when compared with the magnitudes characteristic of alkyledene amines and oximes, is regarded as a consequence of coupling with the unshared electron pair of the neighboring nitrogen atom. By means of the IR spectra, it is possible to determine the position of the double bonds in the pyrazoline ring, to distinguish between pyrazolines substituted and nonsubstituted in positions 1 and 3, and to establish the presence of geminate (twin) methyl groups and methyl groups in position 1.

Until now, the vibration spectra of pyrazolines had not been specially studied, although isolated frequencies had been registered as characteristic in papers dealing with the synthesis of alkyl [1]and aryl [2] substituted Δ^2-pyrazolines. Therefore, the available correlations between structure and vibration spectra, for instance [3], allowed only to assert the presence of double bonds and of N—H groups in pyrazolines. More detailed conclusions as to the structure of these heterocycles (especially their assignment to the Δ^1-, Δ^2-, or Δ^3-series and the determination of the position of the side chains) still remained doubtful. The spectra of a large number (about 30) of alkyl substituted pyrazolines synthesized in recent years [1,4–8] have been compared. This revealed frequencies inherent in the pyrazoline ring and substantiated the prospect of utilizing IR spectroscopy in the structural analysis of this class of compounds.

The valence vibrations of C=N appeared in the IR spectra of Δ^2-pyrazolines as strong or medium bands in the 1580–1627 cm^{-1} region. A sufficiently sharp difference was observed between, on the one hand, the frequency region of the CH=N groups in Δ^2-pyrazolines not substituted in position 3 (1580–1598 cm^{-1}), and on the other hand that of the >C=N groups in 3-alkyl pyrazolines (1620–1627 cm^{-1}). On the whole, the frequency region of $\nu_{C=N}$ characteristic of Δ^2-pyrazolines appeared significantly lower than the 1640–1690 cm^{-1} region assigned in the literature [3] to C=N groups not bound to another by multiple bonds.

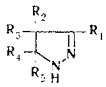


IR Spectra of Δ^2-pyrazolines in the regions of N—H, C—H and C=N valence vibrations: (1) 1-isopropyl-3,4,5-trimethyl-Δ^2-pyrazoline; (2) 1,3,4-trimethyl-Δ^2-pyrazoline; (3) 1-ethyl-5-methyl-Δ^2-pyrazoline; (4) 3,4,5-trimethyl-Δ^2-pyrazoline; (5) 1-methyl-4-ethyl-Δ^2-pyrazoline; (6) 5,5-dimethyl-Δ^2-pyrazoline.

At the same time, it practically coincides with the $\nu_{C=N}$ region (1590–1640 cm^{-1}) in acyclic analogs of Δ^2-pyrazolines, such as the carbonyl compounds of dimethylhydrazones [9]. Evidently, this is a clear manifestation in the electronic spectra of the effect

Table 1

Characteristic Frequencies of the Valence Vibrations in the IR Spectra

of Pyrazolines of Type 

R_1	R_2	R_3	R_4	R_5	ν_{H-N}, cm^{-1}	$\nu_{H-C=}$, cm^{-1}	$\nu_{C=N}$, cm^{-1}
H	H	H	CH_3	CH_3	3290	3050	1588
H	H	H	CH_3	C_2H_5	3270	3040	1588
H	H	H	C_2H_5	C_2H_5	3280	3040	1590
H	H	H	CH_3	n-C_4H_9	3280	3042	1590
H	CH_3	CH_3	H	i-C_3H_7	3305	3045	1598
CH_3	H	CH_3	H	CH_3	3285	—	1625
CH_3	H	H	CH_3	CH_3	3270	—	1626

of bonding with the unshared electron pair of the second nitrogen atom [10]. Comparatively low frequencies of $\nu_{C=N}$ (< 1640 cm^{-1}) are also observed in some other nitrogen heterocycles, such as dihydro-1, 3-thiazines and -oxazines [11]. In Δ-pyrrolidines [12], in which n-π-bonding does not occur, the C=N frequency is also lowered to 1613 cm^{-1}.

Due to their π—π-bonding, Δ^2-pyrazolines with aryl substituents in position 3 may have lowered C=N frequencies [2], and are therefore undistinguishable by this criterion from pyrazolines not substituted in position 3.

The C=N valence vibration bands afford the possibility of distinguishing between Δ^2- and Δ^1-pyrazolines, inasmuch as the N=N vibration of the latter are characterized by much lower frequencies. 5, 5-Dimethyl-Δ^1-pyrazoline exhibits a strong band at 1555 cm^{-1}, attributable to the N=N valence vibrations [5]. This same band (1545 cm^{-1}) was detected in the spectrum of Δ^1-pyrazoline itself [13], as well as in the spectrum of 3, 5-diphenyl-Δ^1-pyrazoline (1548 cm^{-1}) [14]. Therefore, the 1550 ± 5 cm^{-1} frequency may be considered characteristic of the N=N valence vibrations in Δ^1-pyrazolines. In a paper published after the present investigation was completed [15], $\nu_{N=N}$ is given at 1545 ± 5 cm^{-1}. It should be remarked that, in the IR spectra of aliphatic trans-azo compounds, this vibration appears as very weak (often unnoticeable) bands at 1562 ± 5 cm^{-1} [16].

Valence vibrations of H—C=N. Five years ago [1] we recorded the characteristics of the valence vibrations of hydrogen in position 3 of Δ^2-pyrazolines. New experimental data accumulated since then have confirmed that all Δ^2-pyrazolines unsubstituted in position 3 exhibit bands of weak or medium intensity in the 3040–3063 cm^{-1} region. These frequencies are higher than those of the valence vibrations of hydrogen in analogous H—C=C fragments in alkenes (3010–3040 cm^{-1}), but lower than those of the asymmetric valence vibrations of H_2C=C groupings (3075–3095 cm^{-1}).

Table 3

Splitting of the Frequencies of the Symmetrical Deformation Vibrations of Geminate Methyl Groups in Δ^2-Pyrazolines

Compound	δ(S)CH_3, cm^{-1}	
5,5-Dimethyl-Δ^2-pyrazoline	1363	1378
1,5,5-Trimethyl-Δ^2-pyrazoline	1380	1396
3,5,5-Trimethyl-Δ^2-pyrazoline	1365	1378
4,4-Dimethyl-5-isopropyl-Δ^2-pyrazoline	1367	1389
1-Isopropyl-Δ^2-pyrazoline	1372	1385
1-Isopropyl-3-methyl-Δ^2-pyrazoline	1372	1385
1-Isopropyl-4-methyl-Δ^2-pyrazoline	1375	1387
1-Isopropyl-3,4-dimethyl-Δ^2-pyrazoline	1370	1383
1-Isopropyl-3,4,5-trimethyl-Δ^2-pyrazoline	1365	1382
Average value	1371	1385±4

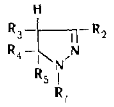
Thus, 1-allyl-4-methyl-Δ^2-pyrazoline has three bands at 3012, 3053, and 3080 cm^{-1}, corresponding to all the indicated hydrogen types. Nevertheless, the difference between these frequencies is small, and apparently their superposition is sometimes possible (1-allyl-Δ^2-pyrazoline exhibits only two bands at 3010 and 3081 cm^{-1}).

3-Alkyl-Δ^2-pyrazolines do not absorb in the 3000–3100 cm^{-1} region.

The valence vibrations of H—N in Δ^2-pyrazolines not substituted in position 1 give rise to fairly broad and intensive bands at 3270–3305 cm^{-1}. This interval borders on the lower limit recorded in the literature [3] for secondary amines in the 3500–3300 cm^{-1} region, but exceeds the ν_{H-N} frequencies in 1,2-dialkylhydrazines (3236 ± 10 cm^{-1}) [16], and in trialkylhydrazines (3164–3185 cm^{-1} according to our data).

Table 2

Characteristic Frequencies of the Valence Vibrations in the IR Spectra of Pyrazolines of Type



R_1	R_2	R_3	R_4	R_5	$\nu_{H-C=}$, cm^{-1}	ν_{CH_3-N}, cm^{-1}	$\nu_{C=N}$, cm^{-1}
CH_3	CH_3	H	H	H	—	2783	1623
CH_3	H	H	H	CH_3	3062	2790	1581
CH_3	H	H	CH_3	CH_3	3066	2805	1595
CH_3	CH_3	CH_3	H	H	—	2785	1620
CH_3	CH_3	H	H	CH_3	—	2782	1623
CH_3	H	CH_3	H	CH_3	3048	2785	1583
CH_3	H	C_2H_5	H	H	3058	2790	1582
C_2H_5	H	H	H	CH_3	3063	—	1587
$(CH_3)_2CH$	H	H	H	H	3062	—	1583
CH_2=$CHCH_2$	H	H	H	H	3080 3010	—	1583*
CH_3	H	H	CH_3	C_2H_5	3060	2795	1580
CH_3	H	CH_3	H	C_2H_5	3050	2790	1588
$(CH_3)_2CH$	CH_3	H	H	H	—	—	1624
$(CH_3)_2CH$	H	CH_3	H	H	3053	—	1583
n-C_4H_9	H	H	H	CH_3	3060	—	1581
$(CH_3)_2CH$	CH_3	CH_3	H	H	—	—	1622
$(CH_3)_2CH$	CH_3	CH_3	H	CH_3	—	—	1618
CH_2=$CHCH_2$	H	CH_3	H	H	3080 3053 3012	—	1582*

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*There is also a $\nu_{C=C}$ band at 1650 cm^{-1}.

No deformation H—N vibrations were observed upon exposure in layers 0.02–0.04 mm thick.

CH_3—N Valence Vibrations are characterized by very strong absorption in the 2782–2805 cm^{-1} region. They are absent in pyrazolines substituted in position 1 not by methyl but by any other substituent or by hydrogen. This band, apparently a low-frequency portion of the Fermi-resonance doublet [17], has been regarded as characteristic of the CH_3—N group in amines and in heterocycles with one nitrogen atom [17, 18]. But its specificity for nonaromatic compounds with a CH_3—N group has been contended [19]. Our data attest to the great specificity of such vibrations in the pyrazoline series.

Deformation Vibrations of CH_3—N in pyrazolines appear as very weak peaks at 1420 cm^{-1} or as shoulders on the intensive bands of the CH_3—C deformation vibrations. These signals are weakly expressed, sometimes inconspicuous, and do not have great diagnostic significance.

$(CH_3)_2C$ Deformation vibrations. In pyrazolines with two methyl groups in position 5, a splitting of the CH_3 symmetrical deformation vibrations band is observed. This is usual in compounds with geminate methyl groups. Such a resonance splitting takes place in all the isopropyl pyrazolines investigated. The $\delta(s)_{CH_3}$ doublet frequencies practically coincide with those indicated for acyclic compounds [3].

EXPERIMENTAL

The spectra were recorded in double-beam IR-10 (Zeiss) and DS-301 (Nippon Bunko) spectrophotometers, using 0.02–0.04-mm thick cuvettes. The Δ^2-pyrazolines were synthesized from unsaturated carbonyl compounds or tertiary acetylene chlorides and hydrazines. Almost all the preparations studied had been described at length in previous papers [1, 4–8]. Tables 1 and 2 present the frequencies of the valence vibrations studied, and Table 3 the frequencies of the symmetrical deformation vibrations of the geminate methyl groups. The figure represents the contours of the absorption bands of representatives of the fundamental structural varieties of Δ^2-pyrazolines in the valence vibrations regions of hydrogen and of the double bonds.

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