SPECTROMETRIC STUDY OF SOME N-SUBSTITUTED 3(5)-METHYLPYRAZOLES AND THEIR COMPLEXES WITH CUPRIC CHLORIDE

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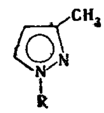
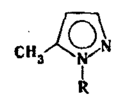
It follows from a comparison of the IR spectra of 1-substituted 3(5)-methylpyrazoles and their complexes with cupric chloride that coordination of the metal is realized through the unshared pair of electrons of the nitrogen atom of the C=N bond.

The number of papers devoted to the study of pyrazoles by vibrational and electronic spectroscopy is limited [1-4]. The accumulation of this sort of data is important for identification purposes and for a study of the effect of substituents on the vibrations and electronic structures of the pyrazole ring. In the present paper we present the results of a spectrometric investigation of 3(5)-methylpyrazole (MP) and its derivatives and of their complexes with cupric chloride. Most of the derivatives were studied in the form of mixtures of two difficult-to-separate isomers, the ratio between which was monitored by chromatography. Some of the physicochemical constants of the described compounds were given in [6]. The spectral characteristics of the investigated substances are presented in Tables 1-3. The experimental assignment of the bands was given in accordance with [1-5, 7].



I a-i



II a-i

I a $R=CH_3$, b $R=C_2H_5$, c $R=n\text{-}C_3H_7$, d $R=i\text{-}C_3H_7$, e $R=n\text{-}C_4H_9$, f $R=i\text{-}C_4H_9$, g $R=i\text{-}C_5H_{11}$, h $R=CH=CH_2$, i $R=CH_2C_6H_5$; II a $R=CH_3$, b $R=C_2H_5$, c $R=n\text{-}C_3H_7$, d $R=i\text{-}C_3H_7$, e $R=n\text{-}C_4H_9$, f $R=i\text{-}C_4H_9$, g $R=i\text{-}C_5H_{11}$, h $R=CH=CH_2$, i $R=CH_2C_6H_5$

An intense band at 3200 cm^{-1}, which vanishes in the spectra of its N_1-substituted derivatives, appears in the spectrum of MP. These bands are related to the stretching vibration of an N−H group tied up in an intermolecular hydrogen bond [1]. The band at 3107-3109 cm^{-1} with a shoulder on the high-frequency side, which appears in the spectra of all of the investigated compounds, evidently is related to the stretching vibrations of the ring =C−H groups. The remaining low-frequency bands between 2830-2980 cm^{-1} are related to the vibrations of methyl and methylene groups of the substituents. The band of a $N-CH_3$ group at 2816 cm^{-1} [7] is characteristic for 1,3- and 1,5-dimethylpyrazoles (I-IIa). Bands of the substituents attached to the nitrogen atom in 1-benzyl-3-methyl (Ii), and in 1-vinyl-3(5)-methylpyrazoles (Ih-IIh) are observed in the 3000 cm^{-1} region at 3088, 3071, and 3032 cm^{-1} for the first compound, and at 3060 cm^{-1} for the last two compounds. The absorption at 1617 and 1500 cm^{-1} in the spectrum of the benzyl derivative (Ii) characterizes the phenyl ring. The frequency of a terminal vinyl group at 1648 cm^{-1} is present in the spectra of vinyl-substituted pyrazoles (Ih-IIh).

The strong absorption band at 1526 cm^{-1} in the spectrum of pyrazole Ia is shifted to higher frequencies (1542 cm^{-1}) for the 1,5-dimethyl isomer (IIa). The same shift (from 1555 to 1532 cm^{-1}) is observed

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TABLE 1. IR Spectra of 1-Alkyl-3(5)-methylpyrazoles (cm^{-1})*

MP	Ia	IIa	Ih	IIh
3200	3121sh	3121sh	3125sh	3118sh
3122sh	3103m	3107m	3110m	3098m
3100w	2972m	2978m	3088vw	3060w
2962m	2928vw	2947	3055w	2985w
1585s	2816w	2882sh	3000w	2925m
1555	1526vs	2818w	2982w	2872w
1543m	1496s	1548s	2955w	2840w
1475s	1445s	1488s	2930m	1650vs
1450s	1408s	1445s	2885w	1555vs
1382s	1395s	1426s	2835vw	1472s
1358s	1295m	1402s	1648vs	1446s
1336w	1281w	1361m	1535vs	1424s
1306w	1213s	1328m	1458m, br	1401w
1280m	1077s	1280s	1425m	1361s
1212m	1041s	1204s	1404w	1330s
1195m	1002s	1177w	1368s	1285s
1050vs	930m	1045s	1345s	1209s
1018s	760vs	1013m	1280s	1120s
1004w	718m	984w	1238w	1041m
940vs		930s	1215sh	1022w
877s		868w	1202s	982w
800s, br		772vs	1072s, br	960s
764vs, br		730m	1038w	922s
			1005w	881vs, br
			980s	782vs, br
			960m	728m
			878vs, br	705m
			758vs, br	
			718m	
			705m	

*Abbreviations: vs is very strong, s is strong, m is medium, w is weak, vw is very weak, sh is shoulder, and b is broad.

TABLE 2. UV Spectra of Methylpyrazoles

Compound	λ_{max}	ε_{max}	Compound	λ_{max}	ε_{max}
MP	215	2440	Id+IId	219	4600
Ia	218	380	Ie+IIe	218	1000
IIa	215	840	If+IIf	219	6100
Ib+IIb	218	1680	Ig+IIg	218	2460
Ib+IIc	219	5100	Ih+IIh	214	10900

on passing from 1-vinyl-5-methylpyrazole Ih to its isomer (IIh). The band at 1525-1530 cm^{-1} in the spectra of the investigated mixtures of N-alkyl-3(5)-methylpyrazoles is expressed more strongly than the band at 1540-1550 cm^{-1}. This is in agreement with the results of gas–liquid chromatography (GLC) regarding the predominance in the samples of isomers with substituents in the 1 and 3 positions. The absorption at 1520-1560 cm^{-1} may probably serve for the determination of the isomerism of 1,3(5)-dialkyl-substituted pyrazoles. In addition to these frequencies, the spectra of all the investigated compounds have an intense band at 1490 cm^{-1}, and it should be assigned to the vibrations of the pyrazole ring [1-5], probably as should the intense band at 1355-1369 cm^{-1}.

A strong band at 1202-1213 cm^{-1}, which in [4] was assigned to the in-plane deformation vibrations of the hydrogen atoms of the pyrazole ring, is also observed in all of the spectra. It seems more probable to ascribe this band to $C-CH_3$ vibrations (as in [5]), inasmuch as this band is absent in the spectrum of pyrazole itself [1]. The band at 758-782 cm^{-1} of the out-of-plane vibrations of the ring C–H bond is distinguished by its special width and intensity [1, 5].

Intense absorption at 214-219 nm (Table 2) is present in the UV spectra. These data differ somewhat from the data presented in [4], possibly because of the use of different types of spectrophotometers. The chain length of the substituent attached to the nitrogen atom has little effect on the position of the absorption maximum. The absorption intensity proved to be more sensitive to the substituent, although a direct relationship between the electronic effect of the substituent and the change in the absorption coefficient is not observed.

The results of a spectrometric study of complexes of N-alkyl-3-methylpyrazoles with cupric chloride are presented in Table 3. In comparison with the spectra of the starting compounds, it was found that the

TABLE 3. IR Spectra of Complexes with N-Substituted 3-Methyl-pyrazoles

$CuCl_2 \cdot 2MP$	$CuCl_2 \cdot 4MP$	$CuCl_2 \cdot Ia$	$CuCl_2 \cdot IIb$	$CuCl_2 \cdot Ic$	$CuCl_2 \cdot Ie$	$CuCl_2 \cdot 2If$	$CuCl_2 \cdot 2Ig$	$CuCl_2 \cdot Ii$
3319s	3230	3154 m	3156 w	3153 w	3153 w	3141m	3148 w	3152 w, sh
3295s	3128s	3132 m	3144 w	3133 m	3133 m	3126s, sh	3134—36 w	3143w, sh
3163m	2991 m	2995	3135 m	2985 s	2983m, sh	3118vw	2970	3131s
3152m	2928m	2950 s	2999 w	2970 s	2971 s	2968vs	2962s	3092w
3138m	2862 w	2925 vw	2979 m	2946 m	2942 m	2936s	2935 w	3066w
2935w	1579s	1546m	2936m	2888 w	2881 m	2878s	2903 w	3030m
1495m	1482m,sh	1506m	1618m	2845 vw	1547 m	2737vw	2876m	2982w
1459m	1450m,sh	1442s	1550	1548s	1501 w	1524s	1548m	2936m
1418m	1430m	1428s, sh	1501m	1500 w	1471m, sh	1506m,sh	1498w	1545 w
1392s	1384w	1402s	1456s	1470m,sh	1462 m	1470m	1473s	1498 w
1365m	1347w	1387m,sh	1406s	1462m	1448 m	1465m	1458s	1456s, sh
1333w	1297s	1366w	1379w	1450m	1407 s	1458m	1416s	1445s
1292vs	1276w, sh	1351w	1356w	1407 s	1384 m	1440m	1372m	1397s
1270s	1221w	1280 s	1317s	1387 m	1343 vw	1430m	1344m	1349m
1257w	1122vw	1208 vs	1284w	1323m	1322 m	1406w	1294s	1329 w
1224s	1051vw	1076 vw	1239m	1304m	1304 w	1380m	1205s	1314m
1115vs	1018m	1024 m	1205s	1280 w	1281 w	1372s	1152vw	1299w
1068m	958s	991 w	1168vw	1234 w	1236 w	1361m	1098w	1221 w
1026m	904m	954 m	1093m	1209s	1210 s	1322m	1047m	1202m
963vs	892m	905 vw	1082w	1177vw	1172 vw	1313m	961m	1194m
910w	793vs	895 vw	1040s	1114 w	1115 vw	1286w	947m	1139m
836m	731m	887 vs	991 w	1097 m	1098 m	1227s	930w	1076w
829s		800 s	956s	1050s	1051 s	1212s	897vw	1062 vw
819s		788 m	891vw	1035m	1037 m	1167vw	839vw	1050 w
790vs		770 m	798s	988vw	956 s	1152 vw	825vw	1027w
718vs		724 m	788s	959s	903 m	1087s	794s	969s
730s				905m	878 w	1047w	764m	943w
				879m	787 s	1009vw	733w	892vw
				790vs	759 w	957 w	723w	846vw
				759m	748 vw	902w		802 s
				738w	725 vw	892		788 m
				723w		879		724 s
						867		698 m
						788vw		
						758w		
						746 w		
						723 w		

TABLE 4. Ratio of Isomeric Pyrazoles (I/II) according to GLC Data

Mixture	I/II ratio, %
Ib+IIb	58 : 42
Ic+IIc	64 : 36
Id+IId	62 : 38
Ie+IIe	63 : 37
Ig+IIg	66 : 34
Ii+IIi	58 : 42

most characteristic changes occur in the region of the stretching vibrations of the =C−H groups of the pyrazole ring and the stretching vibrations of the ring itself. A small shift of a number of bands at 1400-1500 cm^{-1} is observed. Thus the frequencies at 1496 and 1526 cm^{-1} for pyrazole Ia and its complex are shifted to 1506 and 1546 cm^{-1}, respectively. This increase in the frequencies of the vibrations of the azole rings is usually explained in the literature by the formation of donor−acceptor complexes of the σ type [8, 9]. The reaction between the metal ion and the ligand is apparently realized through the unshared pair of electrons of the nitrogen atom of the C=N bond. This is confirmed by the fact of the formation of complexes by substances in which the N_1 atom is sterically blocked by the substituents.

A triplet at 3129, 3141, and 3153 cm^{-1} (the value of the frequencies changes within the limited ±5 cm^{-1} for different substituents) is observed in the region of the =C−H stretching vibrations (at 3106 cm^{-1} for the ligands) for most of the complexes. It is characteristic that a similar, although less pronounced, high-frequency shift of the bands of the vibrations of both the pyrazole ring and =C−H groups is also observed for 4-nitro-1,3(5)-dimethylpyrazoles.

EXPERIMENTAL

The IR spectra of thin layers (in the case of the pyrazoles) and mineral oil and hexachlorobutadiene suspensions (for complexes of the pyrazoles with $CuCl_2$) were recorded with a UR-10 spectrometer. The complete set of frequencies in the IR region of the spectrum is presented only for individual compounds. The method used to prepare the complexes was described in [12]. The UV spectra of 10^{-3}-10^{-4} M solutions of the compounds in n-hexane were recorded with a Beckmann DU-2 spectrophtometer in paired 1-cm thick quartz cuvettes. Analysis by gas−liquid chromatography (GLC) was accomplished with UK-1 or Tsvet-1 chromatographs. Polymethylphenylsiloxane (PMFS-1) on Chromosorb W (20-25% of the weight of the carrier) served as the stationary phase. The column was 2 m long and 4 mm in diameter, the column temperature was 190°, the carrier-gas (hydrogen) flow rate was 3 liters/h. Pure (99%) preparations of the isomers were obtained by separation of the corresponding isomeric mixtures with a column at atmospheric pressure in the case of Ia-IIa, and in vacuo in the case of Ih-IIh. Isomers Ih and IIh were hydrogenated over a Pt catalyst to give Ib and IIb, respectively. The Ib and IIb obtained were identified from the literature data [10, 11]. During GLC analysis the retention times of isomers I were shorter than those of isomers II, and this served as a basis for the identification of the peaks on the chromatograms. The results of GLC analysis of the mixtures are presented in Table 4.

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