IR ABSORPTION SPECTRA OF 1-ARYL-3-PYRAZOLIDONES

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An examination of the frequencies and intensities of the valence vibration bands of carbonyl groups established that the phenyl group interacts with the C = O group of 1-phenyl-3-pyrazolidone and its m- and p-tolyl derivatives in solution. It is assumed that the interaction is accomplished through the N_1 and N_2 atoms in the sp^2 state. 1-Phenylpyrazolidone derivatives are strongly associated in CCl_4 and $CHCl_3$ solutions. The association decreases on passing from CCl_4 to $CHCl_3$ solutions and when there are methyl groups in the ortho positions of the phenyl rings. The energy of association between the 1-phenylpyrazolidones and organic bases (acetonitrile, ethyl acetate, and dioxane), evaluated from the shift in ν_{NH}, is 1.36-3.5 kcal/mole. The frequencies and integral intensities of the bands of the C = O and NH groups in chloroform were measured.

The amide C = O group of pyrazolidones in the crystalline state absorbs at 1960 cm^{-1}, while the NH group absorbs at 3040 and 3140 cm^{-1} [1,2]. On passing to solutions, ν_{CO} increases to 1710-1720 cm^{-1}, while ν_{NH} increases to ~3400 cm^{-1} [1,3,4]. The A_{CO} integral intensity in the IR spectrum of a solution of 1-phenyl-3-pyrazolidone is high [$(5.8-6.9)\cdot 10^4$ liter/mole-cm^{-2}] [2]. In this paper we examine the IR absorption spectra of a number of previously undescribed 3-pyrazolidone derivatives (Table 1).

The CO valence vibration bands in the spectra of the 3-pyrazolidones in the crystalline state lie at 1690-1726 cm^{-1}. The position depends on steric and inductive effects. When there are substituents in the ortho position of the benzene ring, ν_{CO} increases by ~20-30 cm^{-1} in comparison with ν_{CO} in compounds which do not have substituents in the ortho position (Fig. 1, Table 1). When electron-accepting substituents (chlorine atoms) are introduced into the benzene ring, ν_{CO} also increases by 10 cm^{-1}.

The ν_{CO} band in the spectra of solutions of 3-pyrazolidones is observed at 1700-1733 cm^{-1} and has two to three maxima (Fig. 2) which are due to strong associates. Successive dilution of a solution of 1-phenyl-3-pyrazolidone in carbon tetrachloride leads to a decrease in the intensity of the low-frequency component of the ν_{CO} band and to an increase in the high-frequency component. However, the splitting of the ν_{CO} band is preserved in the spectra of dilute solutions in CCl_4 ($1\cdot 10^{-3}$ M). The splitting vanishes only in chloroform on dilution by a factor of ~100 less than in the case of CCl_4, and the symmetrical band remains (Fig. 2, Table 1). This difference in the solvent action can be explained by the much greater capacity of chloroform, as compared with carbon tetrachloride, to disrupt the 1-aryl-3-pyrazolidone associates. The decrease in ν_{CO} by 10-20 cm^{-1} in the spectra of solutions of 1-aryl-3-pyrazolidone solutions in chloroform, as compared with solutions of these compounds in carbon tetrachloride, is due to hydrogen bonds (HB) between the CO group and chloroform.

The ν_{CO} band in the spectra of solutions of 1-phenyl-3-pyrazolidones in CCl_4 and in $CHCl_3$ is higher by a factor of 10-20 cm^{-1} than in the spectra of solutions of 1-cyclohexyl-3-pyrazolidone (1700 cm^{-1}) and γ-butyrolactam (1700 cm^{-1}). Since the ν_{CO} frequencies in the latter two compounds coincide, it can be assumed that the nitrogen atom in the β-position with respect to the CO group in 1-cyclohexyl-3-pyrazolidone does not have an appreciable effect. This is most likely associated with the existence of $N_{(1)}$ in the sp^3

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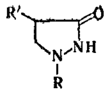
TABLE 1. IR Spectra of 3-Pyrazolidone Derivatives



Compound	R*	Absorption frequencies in KBr pellets, cm^{-1}										In chloroform†					
		ν_{NH}	ν_{CH}	ν_{CH_2}	ν_{CH_3}	ν_{CO}	ν_{Ph}	δ_{CH_2}	δ_{CH_3}	ν_{N-Ph}	ν_{N-C}	ν, cm^{-1}		$\Delta\nu_{1/2}$ cm^{-1}		integral intensity 10^{-4} liter/mole-cm^2	
												C=O	NH	C=O	NH	C=O	NH
I	C_6H_5	3149	3056	2942	—	1695	1606 1504	1472	—	1284	1226	1712	3420	30,0	38,0	5,9	1,11
II	C_6H_5	3151	3052	2958 2926	2966 2870	1692	1604 1496	1456	1456 1390	1316	1203	1711	3421	29,0	39,0	5,9	1,06
III	p-$H_3CC_6H_4$	3140	3032	2915 2860‡	—	1690	1616 1480 1518	1460	1460 1378	1285	1224	1709	3419	29,0	38,2	5,8	1,12
IV	m-$CH_3C_6H_4$	3149	3036	2921 2850‡	2873	1690	1603 1491	1460	1460 1378	1295	1223	1711	3418	29,8	40,0	6,0	1,16
V	o-$CH_3C_6H_4$	3136	3064 3028‡	2928 2850	2968	1726 1650	1608 1584 1530	1460	1460 1360	1309	1206	1703	3418	27,5	37,5	5,5	1,20
VI	2,4,6-$(CH_3)_3C_6H_2$	3160	3080 3050 3015	2921 2850‡	2960 28570‡	1723 1712‡	1595	1467	1467 1372 1363	1315	1200	1700	3420	30,0	32,0	5,4	1,25
VII	o-$CH_3OC_6H_4$	3152	3070	2910 2850	2960 2855‡	1714 1695	1598 1500	1470	1460 1450 1370	1315	1200	1711	3420	30,5	—	5,3	—
VIII	p-ClC_6H_4	3160	3070 3015	2850	—	1704	1602 1512	1470	—	1295	1223	1712	3420	31,5	43,0	5,1	1,22
IX	m-ClC_6H_4	3162	3070 3050	2850	—	1708	1600 1590	1452	—	1315	1200	1718	3418	32,0	44,0	5,05	1,20
X	C_6H_{11}	3159	3068	2851 2926	—	1691	1603 1587	1456	—	1310	1206	1700	3420 3400	31,0	46,0	5,2	1,30

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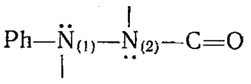
*R' = CH_3 in II, while R' = H in the remaining compounds.

†10^{-2} - 10^{-3} M.

‡Shoulder.

state, which prevents conjugation of the unshared electron pair of this atom with $N_{(2)}$, which is in the sp^2 state [5]. When the hexyl group is replaced by a phenyl group, the $N_{(1)}$ state probably becomes close to the sp^2 state. The conjugated system



$$\mathrm{Ph{-}\ddot{N}_{(1)}{-}\ddot{N}_{(2)}{-}C{=}O}$$

forms as a result. It is well known [6,7] that ν_{CO} increases by 22-33 cm^{-1} on passing from N-alkylamides to N-phenylamides. For 1-phenyl-3-pyrazolidones this effect is lower by a factor of 2 to 3; this may be due to the longer conjugation chain. A confirmation of the manifestation of a conjugation effect through $N_{(1)}$ is the shift in ν_{CO} to the low-frequency region when ortho substituents which remove the phenyl substituents from conjugation are present in the benzene rings (Table 1).

The integral intensity ν_{CO} in the IR absorption spectra of solutions 1-aryl-3-pyrazolidone derivatives in chloroform lies at $(5.0-6.0)\cdot 10^4$ liter/mole-cm^2 (Table 1). When there is an o-methyl group in the phenyl ring, the intensity of the C=O bands decreases somewhat, which is probably associated with a change in the conjugation of the phenyl group in the system due to steric hindrance. A confirmation of this is the closeness of the intensities of the C=O band $(5.2\cdot 10^4$ liter/mole-$cm^2)$ in 1-cyclohexyl-3-pyrazolidone and the intensities of the C=O bands of 1-(o-tolyl)-3-pyrazolidones. The decrease in the intensities of the C=O bands in chloro derivatives of 1-phenyl-3-pyrazolidone is apparently associated with the inductive effect of chlorine.

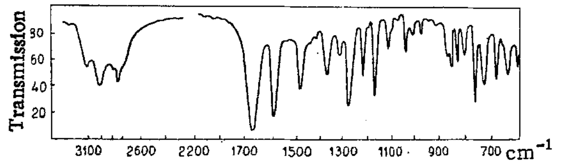


Fig. 1. IR spectrum of 1-(m-tolyl)-3-pyrazolidone (IV) in the crystalline state.

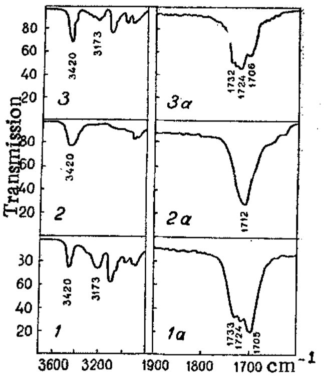
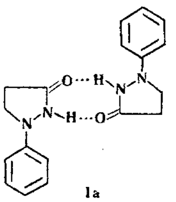


Fig. 2. IR spectra: 1) and 1a) 1-phenyl-3-pyrazolidone (I), c $3.13\cdot 10^{-3}$ M in CCl_4; 2) and 2a) 1-(m-tolyl)-3-pyrazolidone (IV), c $3.12\cdot 10^{-3}$ M in $CHCl_3$; 3) and 3a) 1-phenyl-3-pyrazolidone (I), c $0.78\cdot 10^{-3}$ M in CCl_4.

In the crystalline state the valence vibrational bands of the NH bond are found at 3136-3160 and 2800-3100 cm^{-1}. The shift in the NH bond by 300-500 cm^{-1} attests to a strong HB of the NH···OC or NH···N_1 type. The valence vibration bands of the CH, CH_2, and CH_3 groups in a number of cases are observed as excrescences because of overlap.

Two NH bands at ~3170 and 3420 cm^{-1} are observed in the spectra of solutions of 1-aryl-3-pyrazolidone derivatives in chloroform and in carbon tetrachloride. On successive dilution, the first band vanishes while the intensity of the second band increases to a certain constant value. This sort of behavior of the ν_{NH} band confirms the above assumed intermolecular association of 1-aryl-3-pyrazolidones. The formation of a dimer of the Ia type is most likely from an energetic point of view.



Ia

Steric hindrance prevents the formation of dimers. This is confirmed by the lower intensity of the low-frequency ν_{NH} band in the spectra of V-VII, as compared with the intensity of this band in I-IV, VIII, and IX at the same concentrations and solution layer thicknesses. Dimers are preserved in carbon tetrachloride up to concentrations of 10^{-4} -10^{-5} M. This constitutes evidence in favor of their high stability.

TABLE 2. Energies of HB between 1-Aryl-3-pyrazolidones and Basic Solvents*

Compound	Acetonitrile		Ethyl acetate		Dioxane	
	$\Delta\nu_{NH}$, cm^{-1}	E_H kcal/mole	$\Delta\nu_{NH}$, cm^{-1}	E_H kcal/mole	$\Delta\nu_{NH}$, cm^{-1}	E_H kcal/mole
I	100	1,95	125	2,42	185	3,5
V	95	1,85	116	2,16	165	3,2
VI	70	1,36	90	1,75	160	3,1

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*3% solution of the basic solvent in CCl_4; substrate concentration $\sim 3 \cdot 10^{-3}$ M.

The energy of formation of this sort of dimer is 10 ± 0.3 kcal/mole, according to [8]. Dissociation of these dimers occurs in chloroform at concentrations which, as indicated above, are two to three orders of magnitude higher than in carbon tetrachloride. The energy of the HB of the dimer in $CHCl_3$ is 4.4 ± 0.2 kcal/mole, according to [9]. The difference between the association energies of the dimer in CCl_4 and in chloroform can be taken as the energy of association between 1-phenyl-3-pyrazolidone molecules and chloroform molecules. The elevated value of this difference (5.6 kcal/mole) can be explained by the fact that, with chloroform, 1-phenylpyrazolidones simultaneously give two HB with the C=O and N_1 groups. The energy of the intermolecular HB can be estimated from the formula

$$E_H = \frac{10^2}{k} \frac{\Delta\nu}{\nu} \tag{1}$$

Substituting the above-indicated energy of one CO···HN bond (5.0 kcal/mole) into this formula, we find k = 1.5. Formula (1) can then be used to estimate the values of the HB from the shifts in ν_{NH} in the spectra of solutions of 1-phenyl-3-pyrazolidones in basic solvents. It is apparent from the results obtained (Table 2) that the HB energy increases with increasing basicity of the solvent and decreases in the presence of steric hindrance to conjugation of the phenyl ring with the NH group.

The integral intensity of ν_{NH} of 1-phenyl-3-pyrazolidones in chloroform is $(1.06\text{–}1.30) \cdot 10^4$ liter/mole-cm^2. This is higher by a factor of almost two than the intensity of the ν_{NH} band in amides [10].

EXPERIMENTAL

The investigated compounds (Table 1) were synthesized via known methods [11]; they were recrystallized before the experiments. The IR spectra of the compounds were recorded with a UR-20 spectrometer from 400 to 4000 cm^{-1} in KBr pellets and carbon tetrachloride, chloroform, acetonitrile, acetylacetone, and dioxane solutions. The integral intensities of the absorption bands of the C=O and NH bonds were measured by means of the Burzhen extrapolation method [12] with corrections for shoulders. The solutions were diluted up to $1 \cdot 10^{-3}$ M. The solution layer thickness ranged from 0.1 to 1.0 cm. The accuracy in the measurement of the frequencies of the absorption maxima in the range of an NaCl prism was ± 2 cm^{-1}, compared with ± 6 cm^{-1} in the range of an LiF prism. The accuracy in the measurement of the integral intensities of the absorption bands was ±10%.

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