SPECTRAL MANIFESTATIONS OF STRONG HYDROGEN BONDS IN SEVEN-MEMBERED RINGS OF PYRAZOLECARBOXYLIC ACID DERIVATIVES*

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Strong downward frequency shifts of ν(C=O) of benzoyl or carboxyl group have been found in IR spectra of some pyrazolecarboxylic acid derivatives, and bathochromic shifts of maximum of the first band of $\pi-\pi^*$ transition have been found in their UV spectra, which can be explained by the presence of strong hydrogen bonds in seven-membered rings. Considerable frequency shift of ν(C=O) indicates lowering of order of this bond which is comparable with the bond order lowering of C=O group in six-membered conjugated chelates of the type of enolized β-diketones. In our opinion, formation of strong hydrogen bonds in seven-membered rings in pyrazolecarboxylic acids is due to the presence of the adjoining five-membered aromatic ring, which enables resonance stabilization of the whole π-electronic system in a pseudo-azulene structure.

In our previous report[1] we mentioned strong frequency shifts of ν(C=O) of benzoyl towards lower values in IR spectra of the pyrazolecarboxylic acids prepared by action of diazomethane on (*E*)-3-bromo-4-(4-methoxyphenyl)-4-oxo-2-butenoic acid. It was supposed that these frequency shifts of (C=O) are due to the presence of strong intramolecular hydrogen bonds.

The present paper interprets the yet unpublished experimental data concerning IR and UV spectra of the compounds *I* to *X* and confirming the existence of strong hydrogen bonds in pyrazolecarboxylic acids *I* to *III* and *VII*.

EXPERIMENTAL

The IR spectra of the investigated compounds *I* to *X* were recorded with a UR 20 spectrophotometer (Zeiss, Jena) in KBr discs or in chloroform or dioxane solutions. The spectra of the compounds *I* to *VIII* within 1 500 to 1 800 cm^{-1} in solid state and in solution are given in Figs 1 and 2. For the compounds *IX* and *X* the frequency values of the band maxima within 1 500 to 1 800 cm^{-1} are given. The compound *IX* in KBr disc: 1 512, 1 537, 1 570, 1 601, 1 643 and 1 715 cm^{-1}, and in dioxane solution 1 516, 1 550, 1 570, 1 602, 1 673 and 1 727 cm^{-1}. The compound *X* in KBr disc: 1 509, 1 541, 1 575, 1 601, 1 660 and 1 713 cm^{-1} and in chloroform: 1 516, 1 540, 1 550, 1 579, 1 601, 1 660 and 1 717 cm^{-1}. The UV spectra were recorded with Unicam SP 700 spectro-

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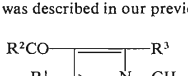
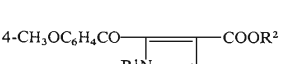
photometer in ethanol and diethyl ether medium. Positions of maxima and values of molar absorption coefficients of the compounds *I* to *X* are given in Table I. Preparation of the used compounds was described in our previous report[1].





I, $R^1 = H$, $R^2 = 4\text{-}CH_3OC_6H_4$, $R^3 = COOH$
II, $R^1 = Br$, $R^2 = 4\text{-}CH_3OC_6H_4$, $R^3 = COOH$
III, $R^1 = H$, $R^2 = OH$, $R^3 = COOH$
IV, $R^1 = H$, $R^2 = 4\text{-}CH_3OC_6H_4$, $R^3 = COOCH_3$
V, $R^1 = R^3 = H$, $R^2 = 4\text{-}CH_3OC_6H_4$
VI, $R^1 = R^3 = H$, $R^2 = OH$

VII, $R^1 = R^2 = H$
VIII, $R^1 = CH_3$, $R^2 = H$
IX, $R^1 = H$, $R^2 = CH_3$
X, $R^1 = R^2 = CH_3$

RESULTS AND DISCUSSION

Infrared Spectra

From the course of the IR spectra of the compounds *I* to *VIII* in Figs 1 and 2 it is obvious that the acids *I* to *III* and *VII* show anomalous behaviour as compared with the rest of the compounds.

For the compounds *I* and *II* the valence vibration band $\nu(C{=}O)$ of benzoyl is found to be shifted from its position at 1641 cm^{-1} for the compound *V* towards lower values *viz.* to 1587 and 1573 (solid) and to 1589 and 1583 cm^{-1} (solution), respectively. The less intensive bands of the compound *I* and *II* at 1608 and 1596 cm^{-1}, respectively, in solid state (in solution the respective values are 1609 and 1603 cm^{-1}) are assigned to valence vibrations of C=C bonds of benzene ring.

Similarly with the solid compound *VII* the $\nu(C{=}O)$ band is found as far as at 1589 cm^{-1}. In dioxane solution an intensive band of the shifted $\nu(C{=}O)$ frequency of benzoyl is seen at 1599 cm^{-1} besides a still lower broad absorption region with inflections at 1610, 1650 and 1670 cm^{-1}.

We presume that the strong frequency shifts of C=O group of benzoyl are due to bond order lowering of this group in a strong resonance-stabilized hydrogen bond in seven-membered chelate between the benzoyl carbonyl group and hydroxyl of carboxylic group of pseudo-aromatic, (pseudo-azulene) structure of type A or B.

This presumption is supported by spectra of the model substances *IV*, *IX* and *X* in which the chelate formation is precluded by esterification, the $\nu(C{=}O)$ frequency of benzoyl being in its usual position *i.e.* at 1657, 1643 and 1660 cm^{-1}, respectively, in solid state, and at 1660, 1673 and 1664 cm^{-1}, respectively, in solution.

In case of the compound *VII* in solution we presume the presence of competing intramolecular hydrogen bond type C or possibly intermolecular hydrogen bonds

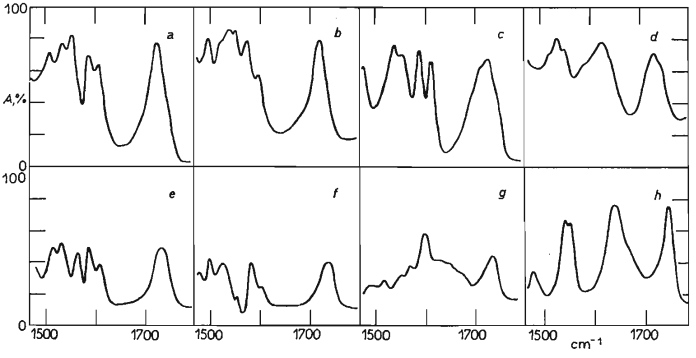


FIG. 1

Infrared Spectra

a, *b*, *c*, and *d* the compounds *I*, *II*, *VII*, and *III*, respectively, in KBr disc; *e* and *f* the compounds *I* and *II*, respectively, in chloroform; *g* and *h* the compounds *VII* and *III* in dioxane.

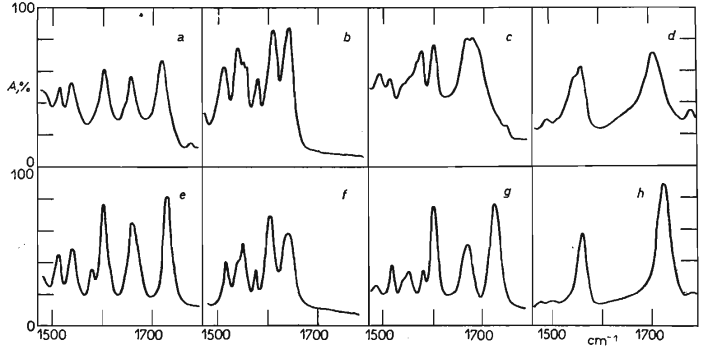


FIG. 2

Infrared Spectra

a, *b*, *c*, *d* the compounds *IV*, *V*, *VIII*, and *VI*, respectively, in KBr disc; *e*, *f* and *g* the compounds *IV*, *V* and *VIII*, respectively, in chloroform; *h* the compound *VI* in dioxane.

between hydroxyl of carboxylic acid group and dioxane, which would explain the broad absorption region at 1600 to 1670 cm^{-1}.

For the dicarboxylic acid *III* we presume a similar seven-membered ring as for the compounds *I*, *II* and *VII*. It could be expected that the diacid *III* would have the valence vibration frequencies ν(C=O) of the both carboxyl groups in one common band. There are, however, two bands here *viz* at 1623 and 1723 cm^{-1} in solid state (1640 and 1748 cm^{-1} in solution). The lower-frequency band is assigned again to the shifted ν(C=O) frequency in the chelate type A. To compare with, the frequency ν(C=O) of the monocarboxylic acid *IV* is found at 1711 and 1723 cm^{-1} in solid state and in solution, respectively.

Further intensive bands of the compounds *I*, *II*, *III* and *VII* in the region 1500, to 1550 cm^{-1} belong to the valence vibrations of double bonds in pyrazole ring, their position and intensity being obviously affected by chelation, too.

No strong chelation takes place in the acid *VIII*, as its benzoyl frequency ν(C=O) is found at usual position *i.e.* 1667 and 1680 cm^{-1} in solid state and in solution, respectively. This fact is obviously due to steric effect of bulky methyl group in position 1, which prevents coplanarity and, hence, resonance stabilization of the system.

TABLE I

Ultraviolet Spectra of the Compounds *I* to *X* in Ethanol and Diethyl Ether Media

Compound	C_2H_5OH		$(C_2H_5)_2O$		Compound	C_2H_5OH		$(C_2H_5)_2O$	
	λ_{max} [a]	log ε [b]	λ_{max}	log ε		λ_{max}	log ε	λ_{max}	log ε
I	220	4·11	215	4·07	*VI*	223	3·99	222	4·02
	287	4·24	285	4·14					
			305	4·22					
II	232·5	4·23	230·5	4·13	*VII*	224[c]	4·01	223	3·88
	277	4·22	268	4·15		294	4·14	308	4·15
			288	4·13		328[c]	3·89		
			298	4·06					
			308[c]	3·99	*VIII*	229·5	4·17	221	4·19
III	240	3·92	249	3·92		297	4·27	290	4·24
IV	225	4·14	219	4·24	*IX*	221	4·16	218	4·20
	291	4·28	276	4·27		292	4·24	283	4·21
			282	4·26					
V	225	4·00	217	4·12	*X*	225	4·20	211·5	4·24
	285	4·26	272·5	4·31		297·5	4·28	293·5	4·27

[a] In nm; [b] in mol^{-1} l cm^{-1}; [c] inflection.

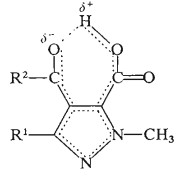
Sterical effect of methyl group disturbing conjugation of benzoyl and pyrazole ring is further documented by the enhanced frequency value ν(C=O) of benzoyl at 1680 cm^{-1}.

Intramolecular nature of hydrogen bonds in the compounds *I* to *III* and *VII* is also supported by the dilution experiment carried out, in which the bands were found in solution at non-changed ratio even at high dilution.

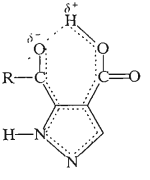
Strong hydrogen bonds in seven-membered rings are also manifested by broad band at 2550 cm^{-1} in IR spectra of the investigated compounds. This band has a number of submaxima due to valence vibration of OH group of carboxyl bonded by hydrogen bond. However, this range was not studied in detail because of its non-specificity. A similar band can be due to carboxylic OH group hydrogen-bonded to nitrogen atom of heterocyclic ring.

Ultraviolet Spectra

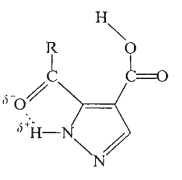
The existence of strong hydrogen bonds in the compounds *I* to *III* and *VII* could be proved by UV spectra, too. With respect to similar effects of the substituents $COOCH_3$ and COOH on the course of UV spectra it could be expected that the spectra of the acids *I* and *VII* would be very similar to those of their esters *IV* and *XI*. This is true in ethanol medium where the difference values in position of the maxima of the first band due to $\pi - \pi^*$ transition in acids and their esters are small, $\Delta\lambda_{max} = -4$ and 2 nm, respectively. However, in diethyl ether medium the first bands of the compounds *I* and *VII* show substantially greater difference of value $\Delta\lambda_{max}$ as compared with their esters, *viz.* 23 and 25 nm, respectively. It is supposed that these bathochromic shifts of the first bands of the acids *I* and *VII* are due to lowered excitation energy in a new chromophore with delocalized electron system in a seven-membered chelate ring. In accordance therewith, the acid *VIII* (which forms no intramolecular hydrogen bond according to IR spectrum) has identical UV spectral course with that of the ester *X*. The absence of bathochromic shift in ethanol medium is explained by disturbance of strong hydrogen bond through interaction of competing hydrogen bonds in solvate shell of solvent.



A



B



C

In the case of the acid *II*, when the respective ester was not at our disposal, the strong chelation was proved on the basis of anomalous solvent effect. The bands of $\pi \rightarrow \pi^*$ transitions show generally a red shift on passing from a less polar to polar medium. In the case of the acid *VIII* and ester *IV*, *IX* and *X* values of these shifts are 7, 9, 9 and 4 nm, respectively, whereas with the acid *II* as well as *I* and *VII* they have an opposite character, *viz.* −31, −18 and −14 nm, respectively, showing thus a blue shift. A similar anomalous shift, revealing the presence of a strong hydrogen bond, is found with the dicarboxylic acid *III* (−9 nm). The monocarboxylic acid *VI* shows the shift value 1 nm.

The effects found in IR and UV spectra of the pyrazolecarboxylic acids (especially the strong shifts in ν(C=O) frequencies) are comparable with the known effects found by Rasmussen and coworkers[2] in six-membered conjugated chelate systems of *e.g.* enolized β-diketones where the hydrogen bonds are stabilized by resonance in a ring of pseudobenzenoid nature.

Our finding of strong hydrogen bonds in seven-membered rings of the compounds *I* to *III* and *VII* agrees well with those in similar compounds: Oae and coworkers[3] proved strong seven-membered intramolecular bonds in furane- and thiophene-2,3- and 3,4-dicarboxylic acids on the basis of anomalously great differences in dissociation constant values of the two carboxylic groups. The authors supported their findings by IR spectra of the componds in solid state, too. They found (as it was the case with the compounds studied by us) that the hydrogen bonds are manifested by a shifted band of one of the carboxylic —C=O groups bonded by hydrogen bond (from the normal position about 1 700 cm^{-1} to the region within 1 650 to 1 620 cm^{-1}) and also by a broad band of a bonded carboxylic —OH group in the region 3 000 to 2 000 cm^{-1}. The existence of hydrogen bond in furane-3,4-dicarboxylic acid was also proved by X-ray studies of its crystal structure[4]. McCoy[5] studied optimum sterical parameters needed for obtaining the maximum strength of hydrogen bond between two carboxylic groups in a series of 1,2-dicarboxylic acids. The author used the difference $pK_E - pK_1$ as a measure of the hydrogen bond strength, K_E and K_1 being the dissociation constants of monomethyl ester and the first dissociation constant of the 1,2-dicarboxylic acid, respectively. In the series of compounds studied by McCoy the strongest hydrogen bond was found with furane-3,4-dicarboxylic acid, in which the optimum sterical parameters are given, in our opinion, by the presence of the five-membered aromatic ring.

The presence of the adjoining aromatic ring, enabling to maintain the optimum length of the hydrogen bridge in a system having a resonance-stabilized pseudoazulene structure, is obviously a condition of formation of strong hydrogen bonds in seven-membered rings in the case of our derivatives of pyrazolecarboxylic acids as well as furane- and thiophene-2,3-and -3,4-dicarboxylic acids.

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