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ELECTRONIC SPECTRA AND STRUCTURE OF CONJUGATE ACIDS OF CARBONYL DERIVATIVES OF PYRROLE

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The nature of the $\pi \rightarrow \pi^*$ transitions in the spectra of neutral molecules of α- and β-formyl-, -acetyl-, and -carbomethoxypyrroles above 210 nm was examined on the basis of an experimental study and calculation by the Pariser–Parr–Pople (PPP) configuration interaction (CI) method. The effect of protonation on the position and intensity of the monotypic transitions was studied. The electronic structures and the energies of the neutral and all of the theoretically possible protonated forms of α- and β-formylpyrroles were calculated within the framework of the CNDO/2 (complete neglect of differential overlap) method. The results of the calculations are in agreement with the experimental data and are in conformity with the greatest energetic advantageousness of protonation of these compounds at the oxygen atom of the carbonyl group.

A study of the protonation of carbonyl derivatives of pyrrole [1, 2] has shown the expediency of the application of UV spectroscopy to the study of the structures of the conjugate acids of compounds of this type.

In order to examine the nature of the $\pi \rightarrow \pi^*$ transitions in the neutral molecules of α- and β-formyl-, -acetyl-, and -carbomethoxypyrroles we measured the spectra of compounds 1-18 (Table 1) above 210 nm in n-heptane and 96% ethanol. We calculated model systems I and II (a, b, and c) and β-acetylpyrroles with different degrees of substitution of the pyrrole ring with methyl groups by the Pariser–Parr–Pople (PPP) method with the Mataga–Nishimoto–Forster parametrization [3, 4] and with allowance for interaction of all of the singly excited configurations. The effective heteroatom model [5] was used in the calculation of the methyl derivatives for the CH_3 group (see following page).

The presence of two absorption bands, the position and relative intensity of which depend on the orientation of the carbonyl group relative to the pyrrole nitrogen atom, is characteristic for the spectra of all of the examined compounds over the investigated range. In the spectra of the β-carbonyl derivatives (Table 1, com-

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TABLE 1. UV Spectra of Carbonyl Derivatives of Pyrrole†

No.	Pyrroles	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$) n-heptane	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$) 96% ethanol
1	3-Methyl-4-acetyl-	260 (3,10) 233 (9,45)	276 (4,37) 248 (12,5)
2	2,4-Dimethyl-3-formyl-	275 (6,65) 243 (13,6)	290 (4,80) 257 (12,7)
3	2,4-Dimethyl-3-acetyl-	268 (4,25) 237 (7,30)	285 (4,54) 253 (9,70)
4	2,4-Dimethyl-3-carbomethoxy-	252 (1,10) 221 (2,00)	261 (5,24) 233 (9,30)
5	1-Ethyl-2,5-dimethyl-3-formyl-	281 (6,20) 250 (10,6)	295 (7,55) 264 (11,7)
6	1,2,4-Trimethyl-3-carbomethoxy-		270 (4,50) 243 (9,18)
7	2,4,5-Trimethyl-3-acetyl-	280‡ 238‡	300 (4,10) 254 (10,2)
8	2,4,5-Trimethyl-3-carbomethoxy-	262 (3,66) 224 (8,45)	272 (4,35) 233 (8,60)
9	2,4-Dimethyl-5-formyl-	296 (19,6) 255 (4,30)	309 (21,4) 270 (4,80)
10	2,4-Dimethyl-5-acetyl-	292 (18,0) 255 (4,00)	306 (9,15) 260 (4,95)
11	2,4-Dimethyl-5-carbomethoxy-	269 (18,3) 245 (4,30)	279 (20,0) 243 (4,60)
12	3,4-Dimethyl-4-formyl-	292 (13,9) 265 (8,50)	304 (15,0) 275 (9,65)
13	3,4-Dimethyl-5-carbomethoxy-	266 (10,2) 246 (7,50)	274 (15,4) 248 (8,10)
14	1,2,4-Trimethyl-5-carbomethoxy-		280 (18,2) 250 (5,40)
15	2,3,4-Trimethyl-5-formyl-	304 (18,1) 265 (6,42)	319 (19,5) 275 (6,30)
16	2,3,4-Trimethyl-5-acetyl-	298 (15,0) 260 (4,90)	316 (19,6) 275 (5,80)
17	2,3,4-Trimethyl-5-carbomethoxy-	281 (14,5) 246 (5,20)	287 (16,6) 250 (4,00)
18	1,2,3,4-Tetramethyl-5-carbomethoxy-	278 (18,0) 254 (8,25)	289 (16,9) 250 (6,20)

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† The spectra of solutions of the compounds [(2–5) · 10^{-5} mole/liter] in quartz cuvettes with a layer thickness of 1 cm were measured with an EPS-3T spectrophotometer.

‡The ε value was not determined because of the low solubility of the compound.

TABLE 2. Theoretical and Experimental Spectra of Methyl-Substituted β-Acetylpyrroles

Compound	Calculated†					Exptl. (n-heptane)	
	$\pi \rightarrow \pi^*$ transitions	λ_{max}, nm	f	predominant configurations	T_c^2	λ_{max}, nm	$\varepsilon \cdot 10^{-3}$
3-Methyl-4-acetylpyrrole	1	259	0,089	$\psi_m \rightarrow \psi_{m+1}$	0,88	260	3,10
	2	241	0,197	$\psi_{m-1} \rightarrow \psi_{m+1}$	0,76	233	9,45
	3	207	0,469	$\psi_m \rightarrow \psi_{m+2}$	0,33		
				$\psi_{m-1} \rightarrow \psi_{m+2}$	0,23		
2,3-Dimethyl-4-acetylpyrrole‡	1	263	0,073	$\psi_m \rightarrow \psi_{m+1}$	0,90		
	2	242	0,032	$\psi_{m-1} \rightarrow \psi_{m+1}$	0,62		
	3	228	0,88	$\psi_m \rightarrow \psi_{m+2}$	0,69		
				$\psi_{m-1} \rightarrow \psi_{m+2}$	0,26		
2,4-Dimethyl-3-acetylpyrrole	1	271	0,223	$\psi_m \rightarrow \psi_{m+1}$	0,94	268	4,25
	2	247	0,197	$\psi_{m-1} \rightarrow \psi_{m+1}$	0,87	237	7,30
	3	212	0,510	$\psi_m \rightarrow \psi_{m+2}$	0,81		
				$\psi_{m-1} \rightarrow \psi_{m+2}$	0,14		
2,4,5-Trimethyl-3-acetylpyrrole	1	280	0,230	$\psi_m \rightarrow \psi_{m+1}$	0,94	280	
	2	252	0,045	$\psi_{m-1} \rightarrow \psi_{m+1}$	0,50		
	3	237	0,890	$\psi_m \rightarrow \psi_{m+2}$	0,49	238	
				$\psi_{m-1} \rightarrow \psi_{m+2}$	0,40		

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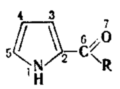
†Symbols: f is the oscillator force, and T_c are the eigenvectors of the configuration interaction matrix.

‡The spectra were not studied experimentally.



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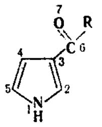


II

a R=H; b R=CH$_3$; c R=OCH$_3$

pounds 1–8) absorption maxima are observed at 250–280 nm (ε 3000–7000) and 220–250 nm (ε 7000–13,000). In the spectra of the α-formyl-, -acetyl-, and -carbomethoxypyrroles (9–18) both transitions are shifted to the long wave region with a change in the relative intensity: λ_{max} 270–304 nm (ε 10,000–20,000) and 240–266 nm (ε 4000–8500). In both series of compounds the increase in the degree of substitution of the pyrrole ring by CH$_3$ groups is accompanied by a successive bathochromic shift of the long-wave band of, on the average, 10 nm.

TABLE 3. Theoretical Spectra of Pyrrole and Its Monosubstituted Derivatives

Pyrroles	$\pi \rightarrow \pi^*$ transitions							
	1				2			
	λ_{max}, nm	f	predominant configurations	T_C^2	λ_{max}, nm	f	predominant configurations	T_C^2
Pyrrole	200	0,02	$\psi_{m-1} \rightarrow \psi_{m+1}$ $\psi_m \rightarrow \psi_{m+2}$	0,60 0,40				
2-Methyl-	212	0,29	$\psi_m \rightarrow \psi_{m+1}$	0,76	197	0,14	$\psi_{m-1} \rightarrow \psi_{m+1}$ $\psi_{m-2} \rightarrow \psi_{m+1}$	0,50 0,29
2-Formyl- (Ia)	256	0,57	$\psi_m \rightarrow \psi_{m+1}$	0,95	224	0,14	$\psi_{m-1} \rightarrow \psi_{m+1}$	0,86
2-Acetyl- (Ib)	232	0,57	$\psi_m \rightarrow \psi_{m+1}$	0,94	213	0,09	$\psi_{m-1} \rightarrow \psi_{m+1}$	0,74
2-Carbomethoxy- (Ic)	242	0,57	$\psi_m \rightarrow \psi_{m+1}$	0,94	217	0,08	$\psi_{m-1} \rightarrow \psi_{m+1}$	0,79
3-Methyl-	218.5	0,19	$\psi_m \rightarrow \psi_{m+1}$	0,73	192	0,18	$\psi_{m-1} \rightarrow \psi_{m+1}$ $\psi_m \rightarrow \psi_{m+1}$	0,60 0,21
3-Formyl- (IIa)	240	0,14	$\psi_m \rightarrow \psi_{m+1}$	0,91	217	0,27	$\psi_{m-1} \rightarrow \psi_{m+1}$	0,89
3-Acetyl- (IIb)	220	0,08	$\psi_m \rightarrow \psi_{m+1}$ $\psi_{m-1} \rightarrow \psi_{m+1}$	0,58 0,22	205	0,34	$\psi_{m-1} \rightarrow \psi_{m+1}$ $\psi_m \rightarrow \psi_{m+1}$	0,55 0,29
3-Carbomethoxy- (IIc)	226	0.08	$\psi_m \rightarrow \psi_{m+1}$	0,74	211	0,34	$\psi_{m-1} \rightarrow \psi_{m+1}$ $\psi_{m-2} \rightarrow \psi_{m+1}$	0,57 0,26

TABLE 4. Contributions of the AO and MO of Pyrrole and Its Carbonyl Derivatives

Pyrroles	ψ_{m-1}		ψ_m		ψ_{m+1}	
	AO (φ_i)	C_i^2	AO (φ_i)	C_i^2	AO (φ_i)	C_i^2
Pyrrole	1,3,4	0,98			1,2,5	0,84
2-Formyl- (Ia)	1,3,4	0,97	2,5	0,67	3,5,6,7	0,85
2-Carbomethoxy- (Ic)	1,3,4	0,97	2,5	0,67	3,5,6,7	0,72
3-Formyl- (IIa)	1,3,4,6	0,78	2,5	0,61	2,3,6,7	0,71
3-Carbomethoxy- (IIc)	1,3,4,6	0,75	2,5	0,56	2,3,6,7	0,57

The theoretical and experimental spectra of methyl-substituted β-acetylpyrroles are compared in Table 2. Calculation for these compounds leads to the presence of two to three $\pi \rightarrow \pi^*$ transitions above 200 nm. The calculated λ_{max} values for both low-energy transitions are in agreement with the experimental values. The results of the calculation satisfactorily reflect the effect of the degree of substitution of the pyrrole ring by methyl groups on the position of these transitions. In addition, neither the number of methyl groups nor their position in the ring has a substantial effect on the character of the configuration interaction. This makes it possible to examine the nature of the electronic transitions in the series of methyl-substituted α- and β-formyl-, -acetyl-, and -carbomethoxypyrroles on the basis of calculation of the spectra of the corresponding model compounds I and II (a, b, and c), which do not contain alkyl substituents in the pyrrole ring. The results of the calculation of the spectra of these models and of unsubstituted pyrrole and its 2- and 3-methyl derivatives are presented in Tables 3 and 4.

Calculation for the carbonyl derivatives of pyrrole leads, in conformity with the experimental results, to the presence of two $\pi \rightarrow \pi^*$ transitions above 200 nm (Table 3). The λ_{max} values observed in the spectra of the investigated compounds 1-18 in n-heptane are shifted 30-40 nm to the long-wave region relative to the theoretical values found for the corresponding model systems; this is evidently explained by the effect of the methyl groups. In addition, the hypsochromic shift of the absorption maxima on passing from α-formyl-, α-acetyl-, and α-carbomethoxypyrroles to the corresponding β derivatives is in qualitative agreement with the experimental data. The trend of the calculated oscillator forces is the same as the trend of the observed ratios of the intensities of the transitions. It follows from the configuration data that we obtained that the long-wave absorption band in the spectra of all of the carbonyl derivatives of pyrrole is due mainly to a one-electron transition from the upper occupied (in the ground state) MO (ψ_m) to the lower vacant MO (ψ_{m+1}). In the series of α-carbonyl derivatives (Ia-c) the contribution of the $\psi_m \rightarrow \psi_{m+1}$ configuration to the first excited state is 94-95%, as compared with 58-91% in the corresponding β-substituted derivatives (IIa-c). The first excited state of unsubstituted pyrrole displays a more complex configuration interaction: two configurations – $\psi_{m-1} \rightarrow \psi_{m+1}$ (~60%) and $\psi_m \rightarrow \psi_{m+2}$ (~40%) – make comparable contributions to the formation of this band. The $\psi_{m-1} \rightarrow \psi_{m+1}$ configuration is predominant in the second excited state of the carbonyl derivatives of pyrrole. With respect to this characteristic and the position in the spectrum (λ_{max}^{calc} 205-224 nm), this transition is formally similar to the first transition in the spectrum of unsubstituted pyrrole. Analysis of the coefficients of ex-

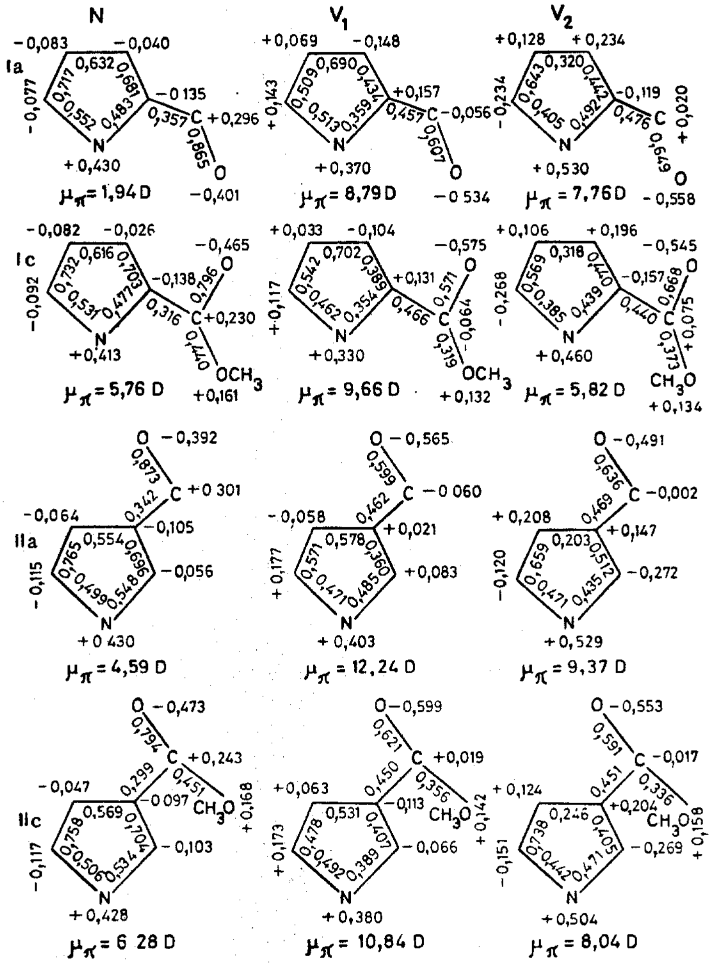


Fig. 1. Molecular diagrams of the ground (N) and first two excited (V_1 and V_2) states of 2- and 3-formyl (Ia, IIa) and 2- and 3-carbomethoxy derivatives (Ic, IIc) of pyrrole (PPP-CI).

pansion of the MO with respect to the AO showed, however, that the contribution of the AO of the carbonyl group (φ_6 and φ_7) to the ψ_{m+1} MO is 40-60% in the series of α-carbonyl derivatives of pyrrole and 20-50% in the series of β-carbonyl derivatives of pyrrole. Since the predominant configurations of the first two transitions in all of the investigated compounds are associated with ψ_{m+1} MO, these transitions do not have direct analogs in the spectra of pyrrole and its alkyl derivatives. In addition, within the limits of the entire series of examined carbonyl derivatives, both of these transitions, respectively, are similar both with respect to the character of the configuration interaction and with respect to the contributions of the AO to the MO of the predominant configurations. It follows from the calculation of the molecular diagrams of the ground and excited states (Fig. 1) that both transitions are related to the transfer of π-electron charge from the pyrrole ring to the carbonyl group of the substituent and are accompanied, as a rule, by a considerable increase in the π component of the dipole moment (μ_π). This effect corresponds to the experimentally observed bathochromic shift of both absorption bands as the polarity of the solvent increases.

The results of a study of the spectra of the neutral molecules make it possible to accurately examine the effect of protonation on the position and intensity of the monotypic electron transitions. It may be assumed that protonation of the α- and β-carbonyl derivatives of pyrrole at the same centers should lead to similar changes in the spectra above 200 nm. The experimental data that we obtained (see Table 5) confirm this assumption. It has been established [1-3] that in aqueous H_2SO_4 solutions 3-carbomethoxypyrroles are protonated exclusively at the α-C_5 atom. Depending on the position of the CH_3 group in the ring, the corresponding 5-substituted derivatives display a capacity for the addition of a proton to both the α-carbon atom and the heteroring nitrogen atom. Protonation in these positions of the pyrrole ring is accompanied by a hypsochromic shift of both transitions; a considerable decrease in the intensity of the long-wave band is also characteristic for 5-

TABLE 5. Spectra of Aqueous Solutions of the Bases and Conjugate Acids of Carbonyl Derivatives of Pyrrole[†]

Pyrroles[‡]	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)		Protonation center
	base	conjugate acid	
1	280 (3,91) 248 (12,6)	330 (2,10) 276 (22,9)	(C)=O
2	295 (4,65) 257 (12,7)	335 (2,30) 272 (19,6)	(C)=O
3	290 (4,70) 253 (9,80)	335 (2,30) 276 (15,9)	(C)=O
4	262 (5,08) 235 (8,96)	252 (5,23)	$C_{(5)}$
5	295 (7,55) 263 (12,0)	335 (2,86) 280 (19,5)	(C)=O
6	270 (5,50) 243 (10,2)	259 (4,10)	$C_{(5)}$
7	300 (4,10) 254 (10,1)	360 (2,92) 277 (18,8)	(C)=O
8	275 (3,59) 236 (6,30)	255 (4,80)	$C_{(5)}$
9	309 (21,5) 260 (4,12)	298 (17,7)	(C)=O
10	307 (20,2) 260 (4,18)	319 (22,0)	(C)=O
11	279 (15,8) 245 (3,00)	253 (4,80)	$N_{(1)}$
12	304 (15,1) 270 (8,60)	340 (5,67) 291 (18,0)	(C)=O
13	275 (15,0) 250 (11,0)	277 (5,00)	$C_{(2)}$
14	280 (18,2) 250 (5,40)	266 (5,34)	$C_{(5)}$
15	319 (19,2) 275 (6,40)	330 (8,65) 293 (15,7)	(C)=O
16	316 (18,6) 265 (4,65)	330 (10,7) 302 (13,9)	(C)=O
17	287 (16,6) 250 (4,00)	263 (5,40)	$N_{(1)}$
18	289 (16,9) 250 (6,20)	278 (5,63)	$C_{(5)}$

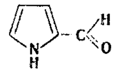
[†] The spectra of the conjugate acids of the investigated compounds in aqueous H_2SO_4 solutions were measured by the method described in [1, 2, 6].

[‡] The numbering of the compounds corresponds to the numbering in Table 1.

carbomethoxypyrroles. Whereas the spectra of the neutral α- and β-carbomethoxypyrrole molecules differ appreciably both with respect to the position and relative intensity of the observed bands, the spectra of the conjugate acids of both series of compounds are extremely similar and are characterized by the presence of a single band of medium intensity at 250-280 nm (ε 4000-5600).

Protonation of the formyl- and acetylpyrroles leads to opposite changes in the spectra: both transitions are shifted to the long-wave region, and the intensity of the first transition is reduced, whereas the intensity of the second increases. These results constitute evidence for a change in the protonation center on passing from carbomethoxypurroles to the corresponding formyl- and acetyl derivatives. It follows from the data from the PMR spectra [2] and the ionization constants [6] that the α- and β-formyl and α- and β-acetylpyrroles are protonated at the oxygen atom of the substituent. Addition of a proton to this center should lead to an increase in the effect of delocalization of the π electrons in the ion as compared with the neutral molecule. The observed changes in the UV spectra on passing from the bases to the conjugate acids are in good agreement with this structure. In the series of β-substituted derivatives the bathochromic shift of the long-wave band is approximately twice the shift of the short-wave band (Δλ 40-60 and 15-30 nm, respectively). The shifts of both bands in the spectra of the α-substituted derivatives are comparable, and the short-wave band experiences a large shift in some cases. This may lead to overlapping of the bands in the spectra of the conjugate acids, for example, in the case of 2,4-dimethyl-5-formyl-, and 2,4-dimethyl-5-acetylpyrroles (Table 5, compounds 9 and 10). However, the sharp increase in the absorption intensity also makes it possible in these cases to sufficiently reliably identify the form that is protonated at the oxygen atom of the carbonyl group.

Thus the study of the electronic spectra and the data obtained by other methods [2, 6] have shown that, in contrast to unsubstituted pyrrole and its alkyl [7, 8], phenyl [9], and carbomethoxy [1, 6] derivatives, α- and β-formyl and α- and β-acetylpyrroles are protonated at the carbonyl group rather than in the pyrrole ring. It was recently established [10] that 3-formyl and 3-acetyl derivatives of 6- and 7-carbomethoxuindolizines are protonated at the same center. In this connection, it seemed of interest to examine the factors that determine the direction of protonation in similar systems. With this in mind, we calculated the electronic structures and energies of the neutral and all of the theoretically possible protonated forms of α- and β-formylpyrroles (Ia and IIa) by the CNDO/2 method with the Pople parametrization [11]. In the calculation we used the data on the geometry of the pyrrole ring presented in [12] and the standard geometrical parameters of the formyl group [13]. Two planar conformations (A, B, C, and D) were calculated for the neutral forms of each isomer: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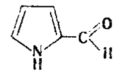
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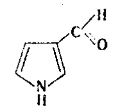
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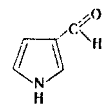

D

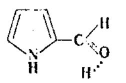
TABLE 6. Change in Energy during the Protonation of α- and β-Formylpyrroles (ΔE, kcal/mole)

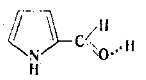
Compound	Protonation center					
	$N_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	(C)=O
Ia	292,8	—	303,3	301,6	306,2	311,4
IIa	294,0	307,7	—	300,4	304,6	314,5

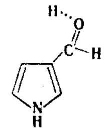
TABLE 7. Distribution of the σ- and π-Electron Densities in the Bases and Conjugate Acids of α- and β-Formylpyrroles

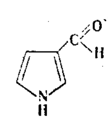
Compound	Form		$N_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	C=(O)	O=(C)
Ia	Base	σ	3,435	2,867	2,986	2,967	2,887	2,934	5,017
		π	1,691	1,096	1,025	1,086	1,039	0,842	1,221
		q_{eff}	−0,126	+0,037	−0,011	−0,053	+0,074	+0,224	−0,238
	Conjugate acid	σ	3,431	2,815	3,046	2,959	2,940	3,033	4,438
		π	1,675	1,179	0,873	1,092	0,900	0,622	1,656
		q_{eff}	−0,106	+0,006	+0,081	−0,051	+0,160	+0,345	−0,094
IIa	Base	σ	3,441	2,886	2,963	2,971	2,872	2,928	5,029
		π	1,675	1,028	1,093	1,074	1,071	0,835	1,225
		q_{eff}	−0,116	+0,086	−0,056	−0,045	+0,057	+0,237	−0,254
	Conjugate acid	σ	3,482	2,945	2,903	2,956	2,878	3,026	4,446
		π	1,595	0,884	1,163	1,069	1,037	0,597	1,654
		q_{eff}	−0,077	+0,171	−0,066	−0,025	+0,085	+0,377	−0,100

The calculation showed a slight difference in the total energies of the conformers: $\Delta E = E_B - E_A = 0.13$ kcal/mole, and $\Delta E = E_C - E_D = 0.35$ kcal/mole. Calculation of the protonated forms was made for the A and D conformations with a lower total energy and the use of the same geometrical parameters as in the case of the neutral molecules. The $>C<^{H}_{H}$ and $>\overset{+}{N}<^{H}_{H}$ angles in the CH and NH conjugate acids were assumed to be tetrahedral (109°30'), and the C−H and N−H distances were assumed to be equal to 1.09 and 1.01 Å, respectively. In the case of the OH acids the calculation was made for two conformers of each isomer:


A_1


A_2


D_1


D_2

The difference in the total energies of the conformers does not exceed 2 kcal/mole, and the A_2 and D_2 conformations are energetically more favorable. The results of the calculation of the energies and electronic structures of the OH acids found for these conformations are presented below.

It follows from the data in Table 6 that the relative basicities of the various centers in 2-formylpyrrole (Ia) decrease in the order $(C){=}O > C_{(5)} > C_{(3)} > C_{(4)} > N_{(1)}$, as compared with the order $(C){=}O > C_{(2)} > C_{(5)} > C_{(4)} > N_{(1)}$ for 3-formylpyrrole. Thus the formation of forms that are protonated at the oxygen atom of the carbonyl group is energetically most favorable for both compounds. This result is in complete agreement with the experimental data. The σ- and π-electron densities and the effective charges (q_{eff}) on the various atoms of the neutral α- and β-formylpyrrole molecules and the corresponding OH conjugate acids are presented in Table 7. The electron density distribution changes substantially during protonation of Ia and IIa, and opposite shifts of the densities of the σ and π electrons are characteristic for most of the atoms. The perturbation produced by the proton is extended to the ring and reaches the atoms four bonds removed from the oxygen atom. An alternation effect is observed. Considerable electron density is delocalized on the added proton. The total π-electron density in the pyrrole ring decreases but increases by a corresponding amount on the carbonyl group. Moreover, there is further polarization of the carbonyl group. The substantial delocalization of the π-electron density from the oxygen atom to the proton, the absolute value of which exceeds the shift of the π electrons, leads to a decrease in the total negative charge on the oxygen atom.

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MOLECULAR AND CRYSTAL STRUCTURES AND CHEMICAL PROPERTIES OF 2,6-DIMETHYL-4-PHENYL-3,5-DIETHOXYCARBONYL-1,4-DIHYDROPYRIDINE

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UDC 548.737+547.827

The molecular and crystal structures of 2,6-dimethyl-4-phenyl-3,5-diethoxycarbonyl-1,4-dihydropyridine were determined by x-ray diffraction analysis. The following crystallographic data were obtained: $a = 9.754(2)$, $b = 7.401(1)$, $c = 24.384(5)$ Å, $\beta = 92.61(2)°$, $Z = 4$, $d_{calc} = 1.24$ g-cm^{-3}, space group $P2_1/c$. The structure was decoded from 1531 reflections, the intensities of which were measured with a $P2_1$ automatic diffractometer and refined by the method of least squares within the total matrix anisotropic approximation to $R = 0.061$. The dihydropyridine ring has a boat conformation. Packing of the molecules in the crystal is realized at the van der Waals distances and is stabilized by an $N_1-H\ldots O_{15}$ hydrogen bond (2.98 Å). From the data on the geometry of the molecule, the compound is closer to aminovinylcarbonyl compounds, whereas according to the data on the conformation, it is closer to Meisenheimer compounds than to pyridine derivatives. The C=O bond length corresponds to its length in esters and acid amides, despite the exceptionally low reactivity of this group in 3,5-dicarbonyl-1,4-dihydropyridines.

To determine the geometry and configuration of the 2,6-dimethyl-4-phenyl-3,5-diethoxycarbonyl-1,4-dihydropyridine (I) molecule and to understand its reactivity we subjected it to an x-ray diffraction study.

The intensities of the reflections were measured with a $P2_1$ automatic four-circle diffractometer using a 0.25 by 0.2 by 0.1 mm light-yellow single crystal. The following crystallographic data on the unit cell of a crystal of the composition $C_{19}H_{23}NO_4$ were obtained by the procedure of autoindexing and calculation of the orientation matrix by the method of least squares (MLS):

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