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Solvatochromism of Heteroaromatic Compounds: XVIII.[1] Reversible Effect of the Medium on the UV spectra of 2-(2-Benzoyl-1-phenylethenyl)-5-phenylpyrrole

V. K. Turchaninov, N. N. Chipanina, Z. V. Stepanova, L. V. Kanitskaya, C. V. Fedorov, G. A. Gavrilova, N. M. Murzina, T. N. Aksamentova, L. N. Sobenina, and A. I. Mikhaleva

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia

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Abstract—Theoretical (B3LYP/6-31G*) and experimental (NMR, UV, and IR spectroscopy) data on the electronic and steric structure of 2-(2-benzoyl-1- phenylethenyl)-5-phenylpyrrole have been analyzed in the context of the hypothesis of the zwitter ionic nature of its ground state. The molecule involves a strong NH···O bond, and its ground state can be described as a hybrid of the neutral and zwitter ionic canonical forms; this conclusion was confirmed by the observation of a reversible medium effect on the electronic absorption spectrum of the substrate.

Solvatochromism of 2-vinilpyrroles containing polar functional groups at the double bond has been described in [1–3]. Extending the range of objects studied we discoved a reversible effect of the medium on the long-wave absorption band in the UV spectrum of 2-(2-benzoyl-1-phenylethenyl)-5-phenylpyrrole (**I**). This effect showed up in a nonlinear dependence of the shift of the bond maximum on the Kamlet–Taft π^* parameter, which has a minimum whose position depends on group properties of solvents. Quantitatively, this effect is weak and has been revealed as a result of systematic research.

The phenomenon of reversible solvatochromism has long been known, but its mechanism is not unclear. There have been attempts to explain it in terms of one- or many-configuration theory with inclusion of medium effects [4, 5]. These studies can hardly been generalized. Moreover, they are not fully adequate to the problem, since ground-state vacant orbitals have been used at both the theory levels. Generally, nonlinear dependences between quantitative characteristics of solvatochromism and medium parameters are associated with dynamic equilibria, solvation-induced variations in the geometry of and electron distribution in solutes, and the attendant dissimilarity in solvent effects on the ground and excited states.

In the present work we dwelt largely on properties of the ground state of pyrrole **I**, particularly in the structural aspect, and obtaining experimental evidence in favor of its zwitter ionic nature, particularly, via the observation of reversible solvatochromism [4, 5].

Qualitative consideration of solvatochromism. Data on the solvatochromism of the long-wave absorption band in the UV spectrum of pyrrile **I** in solvents of different nature are presented in Table 1. In the same place we give Kamlet–Taft general medium parameters. The π^* parameter relates to the ability of the medium to stabilize dipolar electroneutral molecules or ions of the solute (nonspecific solvation). The β parameter quantitatively describes the ability of solvent molecules to act as a proton acceptor in hydrogen bonding with solute.

In the solvatochromistic study we took into account two factors. The electronic absorption spectra of 2-phenylpyrrole derivatives are sensitive to the group solvent parameter δ (roughly measures the polarizability of different groups of solvents [7]) [2, 3]; according to preliminary analysis, the spectra of pyrrole **I** depend on the proton-donor ability α of alcohols.

The results of correlation of ν_{max} and π^* for three groups of solvents with δ 0.0, 0.5, and 1.0 are graphically presented in Fig. 1. As seen, even though the solvatochromism is weak, the correlations between ν_{max} and π^* are all nonlinear.

The π^* values allow the widest variation in the group of aprotic and amphiprotic solvents with δ 0.0.

[*] For communication XVII, see [1].

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Table 1. Solvatochromism of 2-(2-benzoyl-1-phenylethenyl)-5-phenylpyrrole (**I**) in aprotic and amphiprotic solvents

No.	Solvent	Solvent parameters[a]			ν_{max}, cm^{-1}	No.	Solvent	Solvent parameters[a]			ν_{max}, cm^{-1}
		α	β	π^*				α	β	π^*	
			δ 0.0								
1	Hexane	0	0	–0.08	21 500	34	Tetramethylurea	0	0.80	0.83	21 300
2	Pentane	0	0	–0.08	21 500	35	Nitromethane	0.22	0.25	0.85	21 750
3	Heptane	0	0	–0.02	21 500	36	Butyrolactone	0	0.49	0.87	21 550
4	Cyclohexane	0	0	0	21 500	37	Hexamethylphos-	0	1.05	0.87	21 250
5	Isooctane	0	0	0	21 550		phoramide				
6	Octane	0	0	0.01	21 400	38	Dimethylformamide	0	0.69	0.88	21 450
7	Decane	0	0	0.03	21 350	39	Dimethylacetamide	0	0.76	0.88	21 350
8	Dodecane	0	0	0.08	21 300	40	1-Methyl-2-pyrro-	0	0.77	0.92	21 350
9	Decaline	0	0	0.09	21 300		lidone				
10	Triethylamine	0	0.71	0.14	21 400	41	Ethylene glycol	0.90	0.52	0.91	21 550
11	Dibutyl ether	0	0.46	0.24	21 450	42	Dimethyl sulfoxide	0	0.76	1.00	21 450
12	Diethyl ether	0	0.47	0.27	21 550				δ 0.5		
13	Diisopropyl	0	0.49	0.27	21 600	43	Carbon tetra-	0	0	0.28	21200
	ether						chloride				
14	1-Octanol	0.62	0.97	0.37	21 550	44	Tetrachloroethylene	0	0	0.28	21150
15	1-Heptanol	0.64	0.96	0.39	21 500	45	Butyl chloride	0	0	0.39	21 400
16	1-Hexanol	0.67	0.94	0.41	21 550	46	*cis*-1,2-Dichloro-	0	0	0.44	21 450
17	2-Methyl-2-	0.68	1.01	0.41	21 550		ethylene				
	propanol					47	Butyl bromide	0	0	0.48	21 500
18	2-Methyl-2-butanol				21 650	48	Trichloroethylene	0	0	0.53	21 450
19	1-Butanol	0.79	0.88	0.47	21 650	49	Trichloromethane	0.44	0	0.58	21 400
20	2-Propanol	0.76	0.95	0.48	21 600	50	1,2-Dibromo-	0	0	0.75	21 400
							methane				
21	1-Propanol	0.78	0.83	0.52	21 700	51	1,2-Dichloroethane	0	0	0.81	21 500
22	1,2-Dimethoxy-	0	0.41	0.53	21 600	52	Dichloromethane	0.30	0	0.82	21 550
22	ethane										
23	Ethanol	0.83	0.77	0.54	21 650	53	1,1,2,2-Tetrachloro-	0	0	0.95	21 450
24	1,4-Dioxane	0	0.37	0.55	21 550		ethane				
25	Ethyl acetate	0	0.45	0.55	21 650				δ 1.0		
26	Trimethoxymethane	0	–	0.58	21 600	54	Mesytilene	0	–	0.41	21 350
27	Tetrahydrofuran	0	0.55	0.58	21 550	55	*p*-Xylene	0	0.12	0.43	21 400
28	Methanol	0.93	0.62	0.60	21 650	56	Toluene	0	0.11	0.54	21 250
29	2-Butanone	0.06	0.48	0.67	21 700	57	Benzene	0	0.10	0.59	21 300
30	2-Proptanone	0.08	0.48	0.71	21 700	58	Chlorobenzene	0	0.07	0.71	21 300
31	Acetonitrile	0.19	0.31	0.75	21 750	59	Anisole	0	0.22	0.73	21 300
32	Cyclohexanone	0	0.53	0.76	21 400	60	Pyridine	0	0.64	0.87	21 350
33	Propylene carbonate	0	0.40	0.83	21 700	61	Benzonitrile	0	0.37	0.90	21 400
						62	Acetophenone	0	0.49	0.90	21 400
						63	Benzaldehyde	0	0.44	0.92	21 300
						64	Quinoline	0	0.64	0.92	21 300
						65	Benzyl alcohol	0.80	0.50	0.98	21 100
						66	Nitrobenzene	0	0.30	1.01	21 250

[a] See [6].

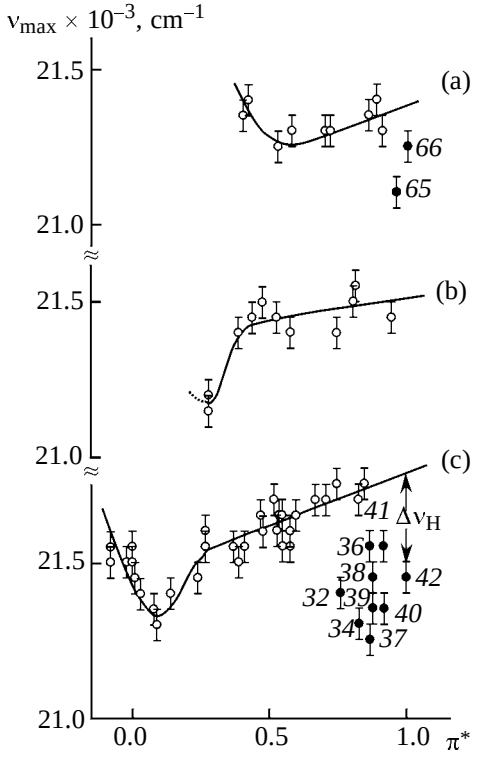
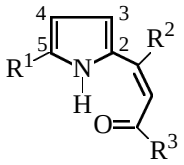


Fig. 1. Effect of solvent polarity/polarizability on the long-wave absorption frequency of 2-(2-benzoyl-1-phenylethenyl)-5-phenylpyrrole (ν_{max}) for δ (a) 1.0, (b) 0.5, and (c) 0.0 [(light circles) $\beta \leq 0.5$ and (dark circles) $\beta \geq 0.5$). Here and in Fig. 1, the solvent numbers are the same as in Table 1.

Here we observe a clearly pronounced reversible solvatochromism (Fig. 1, curve *a*). The observed regularity is violated by only strong H-bond acceptors ($\beta > 0.5$; Fig. 1, curve *a*) with the general parameter $\pi^* > 0.75$.

The phenomenon of reversible solvatochromism is probably characteristic of the group of solvents whose molecules contain an aromatic fragment (δ 1.0, Fig. 1, plot *c*). But here it is obscured by experimental errors, and deviations of points occur at $\pi^* > 0.95$.

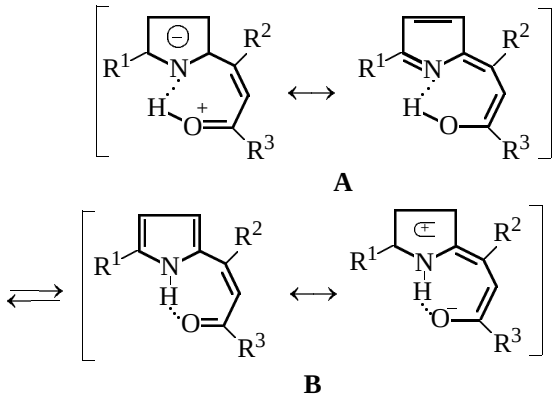


I–VIII

I, $R^1 = R^2 = R^3 = Ph$; **II**, $R^1 = R^3 = Ph$, $R^2 = H$; **III**, $R^1 = R^2 = H$, $R^3 = Ph$; **IV**, $R^1 = R^2 = Ph$, $R^3 = H$; **V**, $R^1 = H$, $R^2 = R^3 = Ph$; **VI**, $R^1 = R^3 = H$, $R^2 = Ph$; **VII**, $R^1 = Ph$, $R^2 = R^3 = H$; **VIII**, $R^1 = R^2 = R^3 = H$.

Tautomerism. The molecules of 2-(2-benzoylethenyl)pyrroles **I**–**III** and other theoretically possible 2-acylpyrrole derivatives **IV**–**VIII** can be present in two tautomeric forms **A** and **B** (Scheme 1).

Scheme 1.



A

B

The ground state of each of the forms can be represented as a resonance hybrid of two canonical structures: neutral (covalent) and zwitter ionic (the positively charged fragment of the zwitter ionic form of tautomer **A** is shown, by analogy with protonated acetone, as an oxonium rather than a carbonium cation [8, 9]).

Nonempirical (HF/6-31G*) calculations for pyrrole **I** and a series of related compounds showed that free tautomer **B** is much more favored by energy (Table 2). Moreover, calculations with different basis sets (6-31G* and 6-311++G**) resulted in close dipole moments (μ_g) of tautomers **A** and **B** in the ground state. Therefore, there are no reason to expect that nonspecific interactions would exert any appreciable effect on their populations. The theoretical predictions are fully consistent with the experimental results in [10–12]. In condensed state (film and solutions in $CDCl_3$ and CS_2), substituted pyrrole **I** and its related compounds exist as tautomer B. This form was found to have quite a high chemical shift of the NH proton (14.7–14.8 ppm) in the ^{1}H NMR spectrum and quite a low N–H stretching vobration frequency (ν_{NH} ~3000 cm^{-1}). Such unusual physicochemical parameters are readily interpreted in terms of the zwitter ionic nature of the compound in study. Nevertheless, some independent evidence is required for firm conclusions, since the above features can also be explained in terms a strong intramolecular hydrogen bond NH···O or N···HO.

Attempts to decide between these two explanations by measuring the dipole moment of pyrrole **I** have not met with success. This experimental value (μ_g 2.26 D; benzene, 25°C) suggests a short arm of the dipole, i.e.

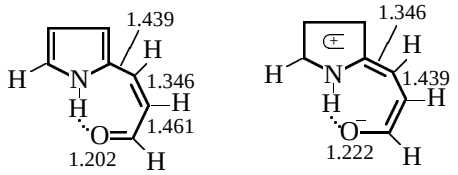
Table 2. Characteristics of the tautomeric forms of 2-(2-benzoyl-1-phenylethenyl)-5-phenylpyrrole (**I**) and 2-formylethenylpyrroles **IV** and **VI**–**VIII** as given by HF/6-31G* nonempirical calculations[a]

Comp. no.	E_t(**B**) – E_t(**A**), kJ/mol	Tautomer **A**	Tautomer **B**				
		μ_g, D	μ_g, D	r_{N-H}, Å	$r_{C=O}$, Å	$r_{N\cdots O}$, Å	∠NH–O, deg
I	–60.6	1.65	1.99	0.999	1.210	2.698	145
IV	–56.0	2.17	2.01	1.000	1.203	2.724	147
VI	–61.6	2.68	2.26	1.000	1.203	2.725	146
VI[b]	–53.2	2.58	2.21	0.999	1.198	2.726	145
VII	–58.9	1.75	1.33	0.999	1.203	2.760	142
VIII	–64.8	2.14	1.61	0.999	1.202	2.762	142

[a]The B3LYP/6-31G* potential energy surface of the tautomeric transformation in the gas phase has no local minimum for form **A**.
[b] HF/6-311++G** method.

the formation of a cyclic structure with an intramolecular hydrogen bond (*Z* stereoisomer). Actually, modeling the zwitter ionic form of compound **VIII** by fixing three carbon–carbon bond lengths at values shown in Scheme 2 (in Å) resulted in a higher dipole moment (by ~1.3 D; HF/6-31G*).

Scheme 2.



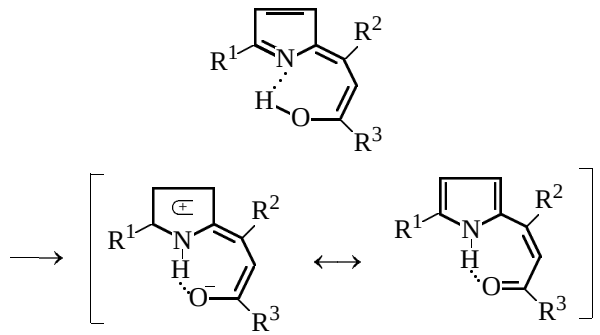
equilibrium strucrure (μ_g 1.61 D) nonequilibrium strucrure (μ_g 2.92 D)

Since the contrubution of the zwitter ionic canonical form in the real structure is lower than 100%, such changes in the μ_g value are of no significance.

Since tautomer **B** with respect to tautomer **A** is a product of intramolecular proton transfer, and the contrubution of the polar form in the ground state of compound **I** is difficult to estimate exactly (if any), it is best to define the most energetically stable form of pyrrole **I** as an intramolecular charge-transfer hydrogen-bonded complex (see also [12]). With such a definition, the role of canonical structures is quite clear (Scheme 3).

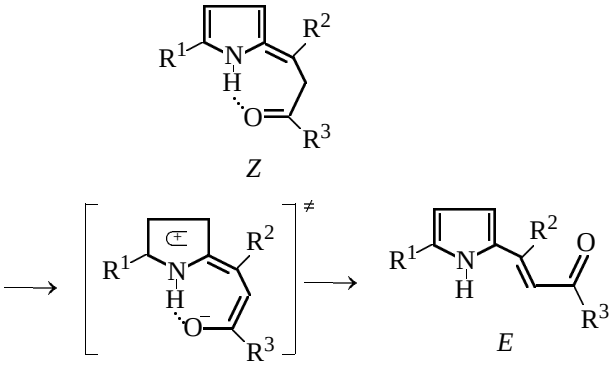
Stereoisomerism. Compounds **I**–**VIII** can exist as two stereisomeric forms (*Z* and *E*) subject to the conversion $Z \rightarrow E$. This process has not been studied in detail, but it is known to be susceptible to the chemical structure of 2-acylethenylpyrroles. There is a suggestion that the facility of the $Z \rightarrow E$ transition is associated with reduced barrier to internal rotation about the C=C bond hich is weakened in the ground

Scheme 3.



state (destabilization of the ground state with respect to transition) [10] (Scheme 4).

Scheme 4.



Z *E*

The role of intramolecular hydrogen bond in stereoisomerism is unclear. On the one hand, it should favor stabilization of the *Z* stereoisomer. On the other, by virtue of the possible synergism of hydrogen bonding and electronic interactions in the π system of 2-acylethenylpyrroles, intramolecular hydrogen bond would favor polarization of the molecule, increasing the contribution of the zwitter ionic structure into its

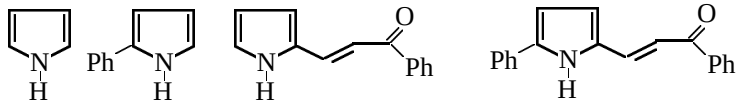
Table 3. Calculated and experimental normal vibration frequencies (ν, cm^{-1}) and bond lengths (Å) of the *Z* isomers of pyrroles **I**–**IX**

Comp. no.	Method	ν_{CH}	ν_{NH}	$\nu_{C=O}$	r_{N-H}	$r_{C=O}$	$r_{N\cdots O}$
I	HF/6-31G*	3336–3460	3792	1910	0.999	1.210	2.698
I	IR, X-ray diffraction	3050–3070	3000	1615	0.99	1.247	2.620
II	HF/6-31G*	3341–3439	3898	1920	0.998	1.209	2.733
II[a]	IR	3050–3070	3286	1639			
IIIa	HF/6-31G*	–	–	–	0.998	1.209	–
Ia[b]	B3LYP/6-31G*	3183–3264	3235	1680	1.031	1.250	2.637
II	B3LYP/6-31G*	3160–3272	3336	1698	1.027	1.248	2.670
III	B3LYP/6-31G*	3158–3281	3358	1703	1.026	1.246	2.643
IV	B3LYP/6-31G*	2967–3287	3235	1714	1.032	1.242	2.658
V	B3LYP/6-31G*	3183–3287	3262	1684	1.031	1.248	2.643
VI	B3LYP/6-31G*	3260–3288	3247	1722	1.031	1.239	2.665
VII	B3LYP/6-31G*	3163–3272	3310	1732	1.028	1.240	2.691
VIII	B3LYP/6-31G*	2962–3282	3327	1738	1.028	1.238	2.696
If[b]	B3LYP/6-31G*	3240–3351	3732	1781	1.009	1.231	–
IXd[b]	B3LYP/6-31G*	–	–	1724	–	1.229	–

[a] Data of [10]. [b] *E* Isomers (Scheme 5).

ground state and thus decreasing the barrier to the $Z \rightarrow E$ transition.

The synergistic effects is readily revealed by comparative analysis of the IR spectra of pyrrole, its model derivatives, and corresponding hydrogen-bonded complexes. Thus, the shift of ν_{NH} produced by the electronic effect of the 2(5)-C_6H_5 and CH=CH–COC_6H_5 substituent in the pyrrole molecule is an additive value (see also references in [13]) and is no more than 40 cm^{-1} throughout the model series in hand.

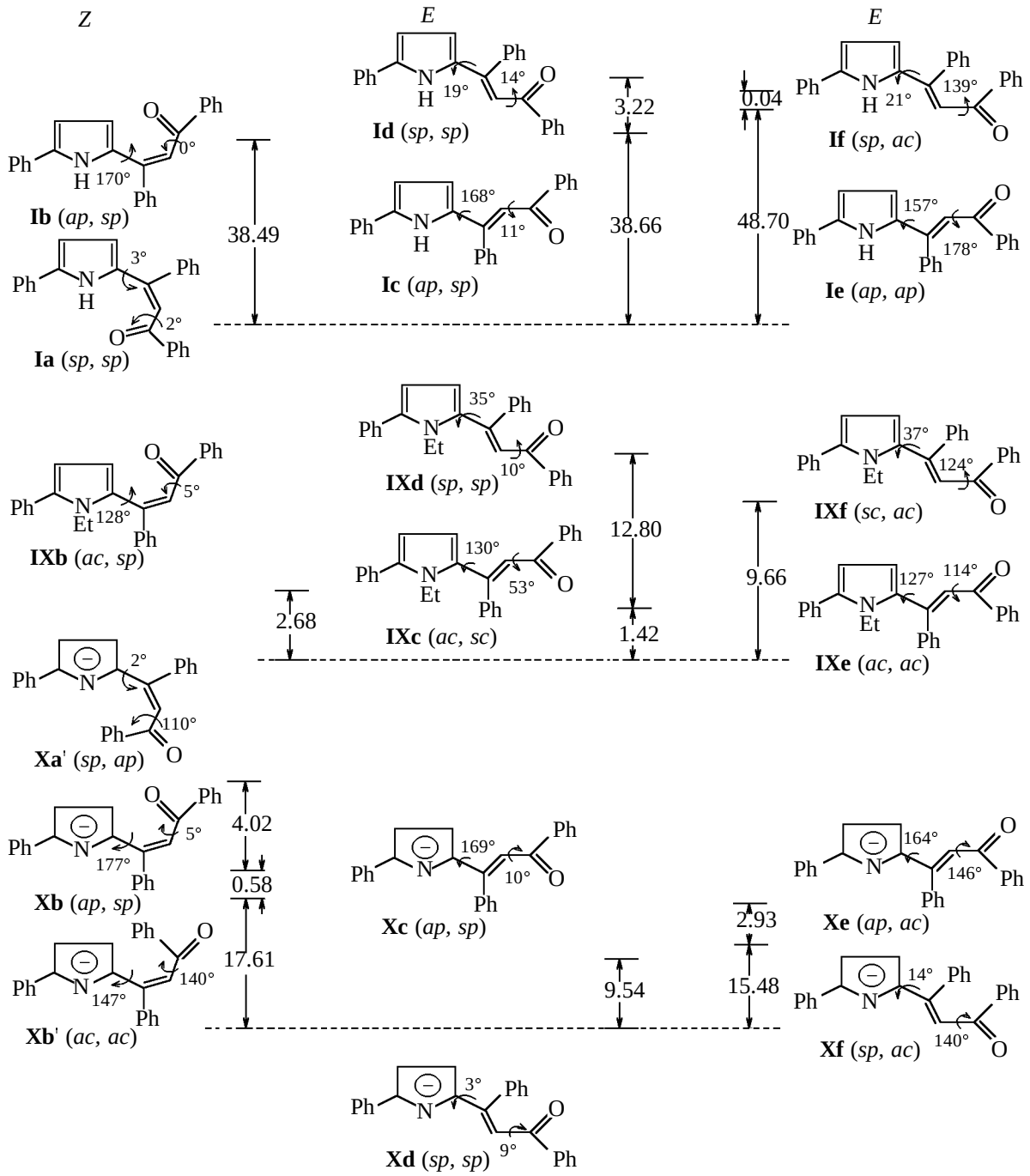


$\nu_{NH}(CCl_4)$, cm^{-1}	3496 [13]	3484	3471 [10]	3460 [10]
ν_{NH}, cm^{-1}	0	12	25	36

The change in ν_{NH} due to intermolecular hydrogen bonding with acetone is 92 cm^{-1} for pyrrole and 67 cm^{-1} for 2-phenylpyrrole, and the respective value for bonding of the latter with acetophenone is 90 cm^{-1}. The N–H stretching vibration frequencies of hydrogen-bonded complexes of pyrrole with such strong carbonyl-containing proton acceptors as DMF and dimethylacetamide are shifted to low frequencies by 140–170 cm^{-1} [13]. Thus, if this vibration frequency is independently affected by substituents and hydrogen bonding, the corresponding bond in the spectrum of pyrrole **I** would be expected at 3350–3250 cm^{-1}. Really its maximum is at ν_{NH} ~3000 cm^{-1} [12].

Since the purpose of the present work was to assess the structure of the ground state of compound **I**, we touched on the problem of stereoisomerism only so far as it concerns the relative stability of the *Z* and *E* isomers and the role of stereisomerism in intramolecular hydrogen bonding. The total energies, geometric parameters, dipole moments, an dnormal vibration frequencies (Table 3) of stereoisomers **Ia**–**If** of compound **I** [Scheme 5; relative energies are given (kJ/mol)] were calculated with inclusion of electron correlation effects (B3LYP/6-31G*). The choice of the calculation method was motivated by the following reasons. This is the only method that fairly re-

Scheme 5.



produces the relative positions of C–H and N–H stretching vibration bands in the IR spectra of the *Z* isomers of compounds **I** and **II** (Table 3). Without inclusion of electron correlation effects, experimental structural and chemical parameters of pyrrole **I** are not reproduced [10, 12] (Table 3).

The Hartree–Fock approximation is unsuitable for calculation of the geometry of molecular systems with a strong intramolecular hydrogen bonding resulting in polarization of the π-electron system of the molecule [14, 15]. The stereoisomery of 2-(2-benzoyl-1-phenylethenyl)-1-ethyl-5-phenylpyrrole (**IX**) (Scheme 5, structures **IXb**–**IXf**) and the anion of pyrrole **I** (Scheme 5, structures **Xa**'–**Xf**), which were considered as models, was studied at the Hartree–Fock level (basis set 6-31G*). As seen from Scheme 5, if intramolecular hydrogen bond is cancelled in any way, the population radically changes in favor of the *E* isomer. Moreover, the *Z* isomer of anion **Xa** which is analo-

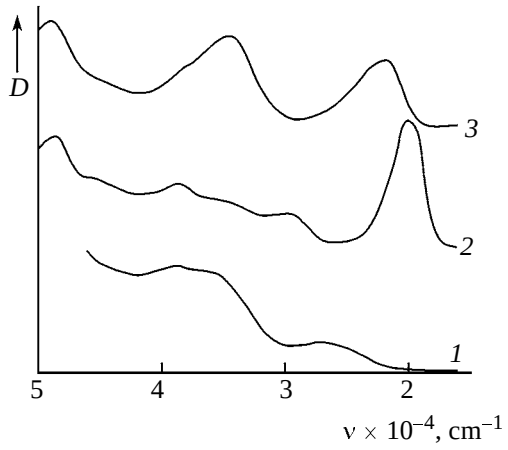
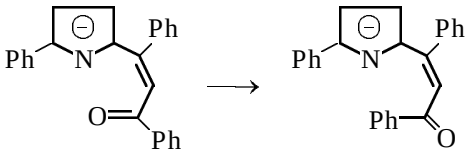


Fig. 2. UV spectra of (*1*) pyrrole **IX**, (*2*) anion of pyrrole **I**, and (*3*) pyrrole **I** in acetonitrile.

gous to the most stable form of the electroneutral molecule, does not exist at all, transforming into its rotamer **Xa'** (Scheme 6).

Scheme 6.



As follows from the calculations, *E* forms of pyrrole **I** with a *cisoid* bond configuration in the acylvinyl fragment (structures **Ic** and **Id**) are 38–42 kJ/mol less favored **by** energy than the most stable *Z* form (structure **Ia**, isolated molecule). Much narrower energy gaps between *E* and *Z* stereoisomers were obtained for pyrrole **III** (HF/6-31G*) (8–13 kJ/mol [10]). Nevertheless, the latter undergoes the $Z \rightarrow E$ transition in the melt only.

The minimal energy effect of intramolecular hydrogen-bonded complex formation with respect to the conformer involving no hydrogen bond was estimated at ~42 kJ/mol (with inclusion of conformational factors). The real energy of H bonding is expected to be slightly higher on account of the deformation of bond angles in the acylvinyl fragment in going from the *ap,sp* to *sp,sp* conformer of the *Z* isomer.

*2-(2-Benzoyl-1-phenylethenyl)-1-ethyl-5-phenylpyrrole (**IX**) and the anion of pyrrole **I** as models of the neutral and zwitter ionic structures.* The calculations show that the *E* isomers of *N*-ethyl derivative **IX** and the anion of compound **I** are stabilized as different conformers [*ac,ac* (**IXe**) and *sp,sp* (**Xd**), Scheme 5] which differ from each other not only by the orientation of the exocyclic double bond with respect to the heteroring, but also by the configuration of bonds in the acylvinyl fragment: *transoid* in pyrrole **IX** (which is consistent with the IR data in [12]) and *cisoid*) in the anion of pyrrole **I**.

By virtue of the nonplanar structure of the *ac,ac* conformer of compound **IX** (Scheme 5) its long-wave absorption band in the UV spectrum is strongly shifted blue with respect to the band of the *Z* isomer of pyrrole **I** (in acetonitrile, $\Delta\nu$ ~5300 cm^{-1}) or with respect to that of the *sp,sp* conformer of anion **Xd** (in acetonitrile, $\Delta\nu$ ~7200 cm^{-1}) and is relatively weak (Fig. 2). Consequently, the pyrrole and acylvinyl fragments in compound **IX** weakly interact with each other by the π-electron mechanism, which makes this compound an adequate model for the neutral form. Two more circumstances favor this choice. First, according to the calculations, its *ac,ac* conformer **IXe** proved to have the shortest C=O bond ($r_{C=O}$ 1.229 Å, B3LYP/6-31G*) among all the pyrroles studied (Table 3), which implies a minor contribution of the zwitter ionic structure. Second, the C=O stretching vibration frequencies in the IR spectra of pyrroles **I** ($\nu_{C=O}$ 1615) and **IX** ($\nu_{C=O}$ 1645) and benzalacetophenone PhCH=CC(O)Ph ($\nu_{C=O}$ 1668 cm^{-1}) [12] proved to be close for the latter two compounds, thus providing evidence showing that pyrrole **IX** belongs to objects with a covalent nature of bonding. The disadvantage of compound **IX** as a model is that it has a different steric structure than pyrrole **I**. However, we failed to find a more adequate model for the neutral form among other compounds of this series. In this connection, in what follows we consider characteristics of pyrrole **IX** as best approximating those of the covalent structure.

The zwitter ion we approximated by the anion of pyrrole **I**, readily generated in a polar, protophilic (aprotic) solvent–MeONa medium. Anion **Xd**, having a *cisoid* bond configuration in the acylvinyl fragment, less differs from pyrrole **I** than the *N*-ethyl derivative of the latter (Scheme 5). However, with its aid we can model only the C^2–C^6=C^7–C^8=O moiety of the zwitter ion.

NMR data. Independent evidence in favor and against the zwitter ionic nature of the ground state of pyrrole **I** can be obtained by ^{13}C NMR spectroscopy [5]. If the real structure is between neutral and zwitter ionic, then the chemical shifts of carbon atoms of the C^2–C^6=C^7–C^8=O chain, sensitive to such effects, should be intermediate between those characteristic of the covalent compound and the anion.

Table 4. Chemical shifts in the ^{13}C NMR spectra (δ_C, ppm) of 2-(2-benzoyl-1-phenylethenyl)-5-phenylpyrrole (**I**), 2-(2-benzoyl-1-phenylethenyl)-1-ethyl-5-phenyl pyrrole **IX**, and the anion of compound **I**

Atom	**IX**	**I**	**I**	Anion
	$CDCl_3$		$(CD_3)_2SO$	
C^2	145.69	150.19	149.82	152.51
C^6	138.78	140.89	139.88	145.11
C^7	109.90	109.52	110.34	106.70
C^8	193.07	189.65	189.51	186.05

Table 5. Solvent effects on the chemical shifts of signals in the ^{13}C NMR spectra (δ_C, ppm) of 2-(2-benzoyl-1-phenylethenyl)-5-phenylpyrrole (**I**) (26°C)

Solvent	C^2	C^6	C^7	C^8
CCl_4	150.51	141.2	109.95	188.96
Chloroform-*d*	150.19	140.86	109.52	189.65
Methylene chloride	150.62	141.08	109.92	190.03
DMSO-d_6	149.82	139.88	110.34	189.51

The ^{13}C NMR spectra of pyrroles **I**, **IX** and the anion are listed in Table 4. As seen, the strongest variations are characteristic of the C^2 and C^8 chemical shifts, and, therewith, the δ_C values for compound **I** are intermediate between those for the anion and compound **IX**. In going from pyrrole I to its 1-ethyl derivative, the chemical shift of the heteroring C^2 atom decreases by 4.5 ppm (from 150.2 to 145.7 ppm). At the same time, 1-alkyl substitution in pyrroles most commonly produces deshielding of C^2 and C^5 and, as a result, shifts the corresponding signals downfield by ~5–7 ppm [13, 16]. This finding implies that the five-membered ring in pyrrole I is markedly polarized, and thus the electron density on C^2 changes in the opposite direction. However, in interpreting the above observation one should not exclude direct effects of formation in pyrrole **I** of a fairly strong hydrogen bond. The resonance signal of the carbonyl carbon in the ^{13}C NMR spectrum of pyrrole **I** is shifted upfield relative to the respective signal of *N*-ethyl derivative **IX** by 3.5 ppm. Note that intramolecular hydrogen bonding usually produces the opposite effect: The carbonyl carbon signal shifts slightly downfield [17]. For this reason, the upfield shift of the carbonyl resonance signal of pyrrole **I** in going to the model *N*-ethyl derivative can be considered as indirect evidence in favor of the zwitter ionic nature of the ground state of **I**. Further evidence for this conclusion comes from a comparison of carbonyl chemical shifts of the neutral molecule and the anion.

The contribution of the zwitter ionic structure into the ground state of pyrrole **I** is further supported by the unusual behavior of its C^2 signal, which can be explained in terms of the electronic effect of the 2-substituent in the pyrrole ring. Thus, for instance, in the ^{13}C NMR spectrum of compound **II** (*E* isomer) the signal of the C^2 atom that bears the CH=CH·C(O)Ph substituent is at δ_C 140.13 ppm. Given are solvent: compound (δ_{C^2}, ppm): $CDCl_3$: 2-phenylpyrrole (131.83), **II** (140.13), **I** (150.19); $CDCl_3$ + triethylamine: 2-phenylpyrrole (132.07), **II** (140.04).

α-Phenyl substitution in the CH=CHC(O)Ph substituent (pyrrole **I**) produces an unexpectedly strong downfield shift of the C^2 signal (by 10.06 ppm). Such a strong shift is impossible to explain in terms of intramolecular hydrogen bonding. Thus, addition to solutions of 2-phenylpyrrole and pyrrole of such a strong hydrogen-bond acceptor as triethylamine does not appreciably affect the C^2 chemical shifts of these compounds.

Thus, the great differences in the UV, NMR, and IR spectra of compounds **I** and **IX** should be interpreted as a consequence of the formation of a strong intramolecular bond in the former, accompanied by a considerable π-electron density redistribution. Since the state of the hydrogen bond in solution would be determined by the model and by solvation effects, we considered it expedient to measure the ^{13}C NMR spectra of pyrrole **I** in various media (Table 5). The trend in the carbonyl chemical shifts proved unexpected: As the nonspecific solvation grew in the order $CCl_4 < CDCl_3 < CH_2Cl_2$, the C=O signal slightly but systematically shifted downfield, i.e. to the region characteristic of the covalent structure. At the same time, the highly polar DMSO which is a strong hydrogen-bond acceptor did not fit in the observed trend. These results allow a simple and consistent interpretation: The contribution of the zwitter ionic structure into the ground state of pyrrole **I** decreases with increasing polarity of a nonspecifically solvating halogen-containing hydrocarbon solvent and increases if the specific solvation mechanism is operative. Consequently, the expected stabilization of the more polar form of the solute in a more polar medium does not occur, but the hypothesis on the effect of a strong intramolecular hydrogen bond in the electronic structure of pyrrole **I** gains substantiation.

Nonspecific and specific effects of the medium in the electronic absorption spectrum of 2-(2-benzoyl-1-

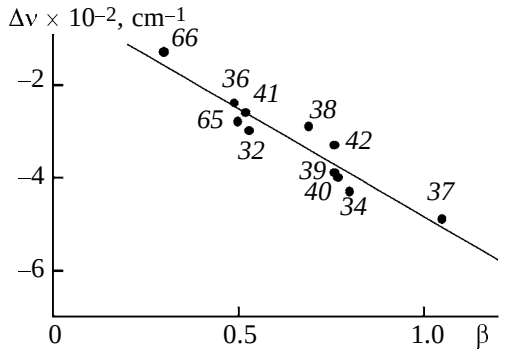


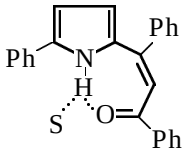
Fig. 3. Plot of spectral shift vs. proton-acceptor ability of solvent.

phenylethenyl)-5-phenylpyrrole (I). In the analysis of solvatochromistic details in a group of halogen-containing hydrocarbons with δ 0.5 we took account of the following facts: The long-wave absorption band of the anion of pyrrole **I** is shifted to lower frequencies compared with pyrrole **I** (Fig. 2). According to the NMR data, the contribution of the zwitter ionic form into the ground state of pyrrole **I** slowly decreases with enhancing ability of solvents to nonspecific solvation, i.e. with increasing π^*. In view of the aforesaid, a blue shift of the absorption band would be expected. This proved the case (Fig. 1, plot *b*).

The points corresponding to strong hydrogen-bond acceptors with $\pi^* > 0.75$ shift to lower ν_{max} in the UV spectrum ($\beta > 0.5$; Fig. 1, plot *a*), i.e. to the range characteristic of ionic forms, as expected by the NMR data. Deviation of points at δ 1.0 (Fig. 1, plot *c*) is observed at $\pi^* > 0.75$.

To find out reasons for these deviations, we made use of the method of spectral shifts (Δν in Figs. 1 and 3). Even though the approximation is rough, it proved that Δν increases in absolute value with increasing β (Fig. 3). In other words, the deviation of points is associated with the formation between the solute and solvent of a hydrogen-bonded complex possessing specific solvatochromic parameters. It will be emphasized that specific interactions with solvent cause no structural changes in compound **I** (rotational isomerism and $Z \rightarrow E$ transition); otherwise, the absorption band would has shifted blue. Consequently, specific solvation of pyrrole **I** is effected by formation of a complex with a three-center (bifurcate) hydrogen bond (Scheme 7; S is solvent). This process takes place in media whose polarity and proton-acceptor ability has attained some "threshold" values, which is untypical of solvation complexes with a two-center hydrogen bond [6, 18–20].

Scheme 7.



The spectroscopic consequence of the formation of a solvation complex with a three-center hydrogen bond is a red shift of the absorption band, i.e. to the range characteristic of the anion. The same effect we earlier observed [2, 3] with similar solvation complexes with an NH–π system intramolecular hydrogen bond.

EXPERIMENTAL

The IR spectra of compound **II** and 2-phenylpyrrole in CCl_4 containing acetone or benzophenone additives were obtained on a Specord IR-75 spectrophotometer. The UV spectra of pyrrole **I** were taken on a Specord UV-Vis spectrophotometer in a wide range of solvents (Table 1).

The ^{13}C NMR spectra of compounds **I**, **II**, and **IX** were run on Varian VXR-500S (125.5 MHz) and Bruker DPX-400 (100.6 MHz) spectrometers, internal reference HMDS.

Nonempirical calculations of molecules **I**–**IX**, as well as the gas-phase vibration spectra of the latter and the anion of pyrrole **I** were calculated using the GAUSSIAN 98 program package [21].

The methods of synthesis of 2-(2-benzoyl-1-phenylethenyl)-5-phenylpyrrole (**I**), 2-(2-benzoylethenyl)-5-phenylpyrrole (**II**), and 2-phenylpyrrole are described in [10, 11, 22].

2-(2-Benzoyl-1-phenylethenyl)-1-ethyl-5-phenylpyrrole (IX). A mixture of 0.0856 g of 1-ethyl-2-phenylpyrrole, 0.103 g of 1-benzoyl-2-phenylacetylene, and 2 g of SiO_2 (100/160 μm) was heated for 4 h at 90°C with intermittent shaking. The reaction mixture was applied to a column of Al_2O_3 and eluted with a 3:1 hexane–ether mixture to isolate 0.101 g (54%) of pyrrole **IX** as an oily, yellowish-orange substance. Found, %: C 85.97; H 6.39; N 3.48. $C_{27}H_{23}NO$. Calculated, %: C 85.91; H 6.14; N 3.71.

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