The effect of the physical state on the equilibrium conformation of 2-arylpyrroles

V. K. Turchaninov, A. I. Vokin, and S. E. Korostova*†

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
1 ul. Favorskogo, 664033 Urkutsk, Russian Federation.
Fax: 007 (395 2) 46 6425

The equilibrium torsion angles of 2-arylpyrroles in the liquid and solid phases were estimated by UV spectroscopy. In solution, compounds containing no substituents in positions 1, 3, and 2′ possess an average torsion angle of 24°, those containing one substituent have an angle of 29°, and in the case of two and three substituents, the angles are 53° and 65°, respectively. Phase transitions lead to flattening of the molecules in almost all cases. The average torsion angles in the compounds with no substituents in positions 1, 3, and 2′ decrease by ~5° on passing from the gas to the liquid state and by ~25° on going from the liquid to the solid state. The geometric parameters of 2-arylpyrroles with one or two substituents in positions 1, 3, and 2′ are less sensitive to phase transitions, while trisubstituted derivatives even retain their equilibrium conformations upon phase transitions.

Key words: equilibrium conformation of molecules, UV spectroscopy, semiempirical MO calculations, 2-arylpyrroles.

Of conformationally mobile molecules with extended π-systems, diphenyl and its derivatives have been structurally studied in greatest detail. The equilibrium geometry of these compounds depends markedly on the nature of the substituents and on the physical state. For example, the equilibrium torsion angle in diphenyl varies from 44° in the gas phase[1] to 30° (or 20°)[2,3] in the liquid phase and to 0° in the crystal.[4] The conformations of a fairly large number (~20) of diphenyl derivatives having no substituents in the *ortho*-positions of the phenyl groups are susceptible to similar influences.[5] This is due to the fact that rotation of phenyl groups requires relatively little energy, which can be made up by intermolecular interactions.[6] The conformations of other linked cyclic systems also depend on the physical state. One of the few known examples of this dependence is 3,3′-dithienyl, whose equilibrium torsion angle is 30° in the gas phase,[7] 22° in the nematic phase,[8] and 0° in the crystal.[9] Structural studies of the vast majority of compounds of the diphenyl type have been carried out for one of the physical states.[10—12] In particular, we determined the equilibrium torsion angles for a series of 2-phenylpyrroles (2-PP) in the gas phase by photoelectron spectroscopy.[13—16] Almost all of these compounds were found to be non-planar. In the present work, the equilibrium conformations of 2-arylpyrroles in solution and in a solid matrix were studied by UV spectroscopy.

Experimental

Electronic absorption spectra were recorded on a Specord M-40 spectrophotometer at 22—25 °C. The concentrations of compounds in hexane and acetonitrile amounted to 10^{-4}—10^{-3} mol L^{-1}. The spectra in the solid phase were recorded in poly-(1-vinyl-2-methylimidazole) (PVMI) films and in KCl discs. The first procedure makes it possible to obtain more precise information on the positions of long-wavelength bands (Fig. 1); addition of PVMI has no effect on the UV spectra of the compounds in solution. However, this procedure is inapplicable to diphenyls, since the allowed $S_0 \rightarrow S_2$ transition is not manifested in the spectra recorded in thin films; instead, the forbidden $S_0 \rightarrow S_1$ transition is recorded.[3]

Emission spectra were obtained at an angle of 45°. A crystalline sample of 2-phenylpyrrole was prepared by spraying it onto a transparent support *in vacuo*.

To calculate the energies of transitions in the UV spectra and to study their dependence on the torsion angle, the CNDO/S method was used.[17] The calculations in this approximation were based on geometric parameters found by MINDO/3 optimization for each particular angle.[18] The optimization was performed for all geometric parameters except for the bond lengths and angles in the benzene ring. Torsion angles were specified with a step of 15°. Geometric parameters of the benzene ring were found from the equilibrium structure of the molecule. In the case of *N*-vinyl-2-phenylpyrrole, parameters of the vinyl group and the angle determining its spatial arrangement were also optimized.

The pyrroles for the investigation were synthesized by known procedures;[19,20] their melting points corresponded to the reported values.[19] Crystalline compounds were purified by sublimation, and liquids were distilled *in vacuo*. The purity of

---

† Deceased.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1472—1479, August, 1997.

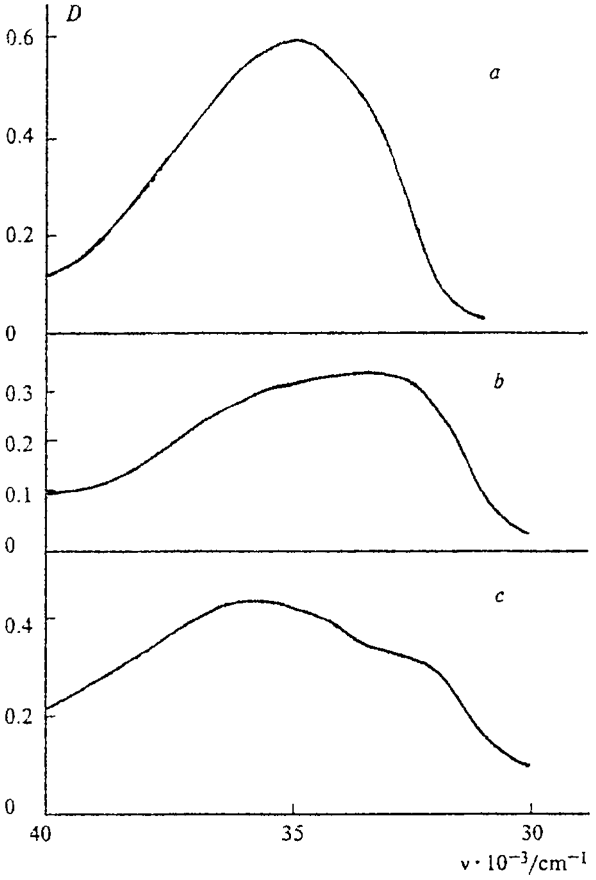


Fig. 1. Long-wavelength absorption band of 2-PP in a solution in MeCN (*a*), in poly-(1-vinyl-2-methylimidazole) film (*b*), and in KBr disc (*c*).

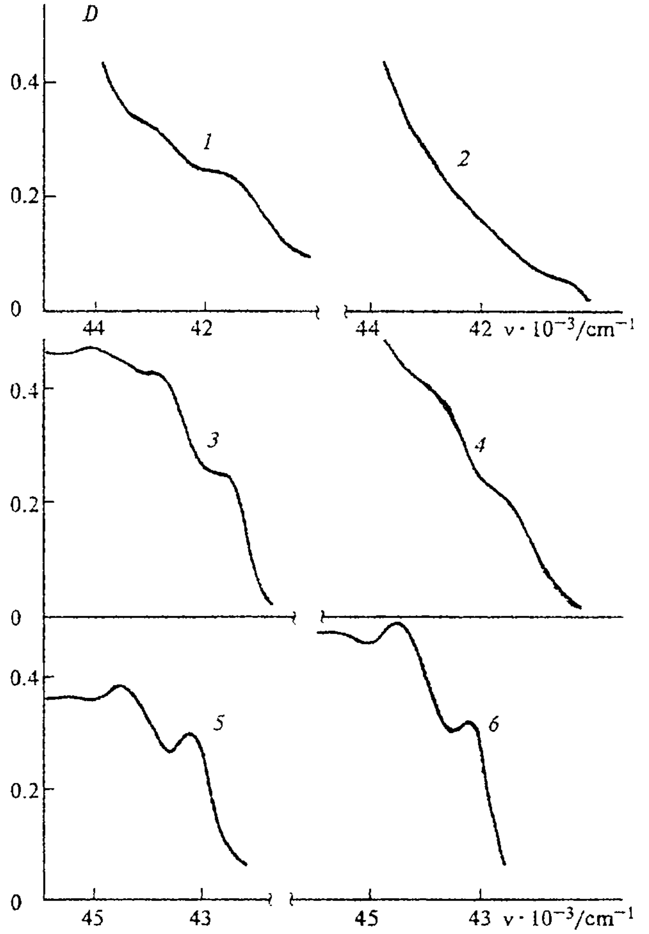


Fig. 2. Short-wavelength absorption band of 2-arylpyrroles in hexane: 3-ethyl-2′,5′-dimethyl-2-PP (*1*), *N*-ethoxyethyl-3-ethyl-2′,5′-dimethyl-2-PP (*2*), 5-methyl-2-PP (*3*), 3-*n*-nonyl-2-PP (*4*), 2-PP (*5*), 4′-methyl-2-PP (*6*).

the products was checked by TLC on Silufol UV-254 plates (hexane—ether, 3 : 1). Spectral characteristics of some of the studied pyrrole derivatives in hexane and acetonitrile are fairly close to those found previously for solutions in cyclohexane and ethanol.[19]

Results and Discussion

2-Arylpyrroles. In the region of $\lambda > 210$ nm, the UV spectra of 2-arylpyrroles containing no unsaturated substituents consist of two absorption bands in the 220—240 and 260—290 nm ranges (Figs. 1 and 2, Table 1). According to CNDO/S calculations, the contour of these bands envelopes three components (Table 2).

The electron transition ($S_0 \rightarrow S_1$) determining the intensity and position of the longest-wavelength band is a singe-configuration transition (see Table 2) that causes redistribution of charge between the rings. The other component of this band is due to the $S_0 \rightarrow S_2$ transition ($^1B_{2u} \leftarrow {}^1A_{1g}$ in the local symmetry of the benzene moiety). In a real spectrum, this component is normally covered by a band corresponding to the $S_0 \rightarrow S_1$ transition or is exhibited as a shoulder (4,5-dihydrobenzo[g]indole (DHBI), 2-PP, 3-methyl-2′,5′-dimethyl-2-PP, and 1-ethoxyethyl-3-ethyl-2′,5′-dimethyl-2-PP). Only in the spectrum of 2-PP recorded in a KCl disc, does the $S_0 \rightarrow S_2$ transition account for the most intense peak (see Fig. 1). The position of the longest-wavelength band of 2-arylpyrroles is appreciably affected by substituents (see Table 1). Even alkyl groups, which usually have almost no effect on the positions of absorption maxima in the UV spectra of fused aromatic compounds,[21] often cause substantial shifts of this band with respect to that in the UV spectrum of 2-PP. The direction of these shifts depends on the positions of substituents. In fact, replacement of hydrogen in positions 4′ or 5 by a methyl group either has no effect on the spectrum in solution (4′-methyl-2-PP) or leads to a bathochromic shift of the band in question (5-methyl-2-PP). Conversely, the presence of alkyl substituents in positions 1, 3, or 2′ results in substantial (up to 2400 cm^{-1}) hypso-

Table 1. Characteristics of $\pi \rightarrow \pi^*$ transitions in the UV spectra (ν/cm^{-1}) of 2-arylpyrroles

Compound	Solvent	$S_0 \rightarrow S_1$	$S_0 \rightarrow S_3$		
2-PP	Hexane	34700[a]	43250	44600	45700
	Acetonitrile	34900	43300 sh	44800	45800 sh
	PVMI[b]	33600		44500 sh	
4′-Methyl-2-PP	Hexane	35300[a]	43300	44550	45600
	Acetonitrile	35000	43300 sh	44800	45600 sh
	PVMI[b]	34100			
4′-Fluoro-2-PP	Hexane	35850	43700 sh	45000 sh	46000 sh
	Acetonitrile	35400	43600 sh	45100 sh	
	PVMI[b]	34650			
4′-Chloro-2-PP	Hexane	34000[a]	42900	44300	45000
	Acetonitrile	34100	43000 sh	44800	45600 sh
	PVMI[b]	33200		44500 sh	
4′-Bromo-2-PP	Hexane	33800[a]	42700 sh	44000	45200 sh
	Acetonitrile	33800	42600 sh	44500	45200 sh
	PVMI[b]	33000			
4′-Phenyl-2-PP	Acetonitrile	31900	43000—44000		
5-Methyl-2-PP	Hexane	33500[a]	42600	44000 sh	45200
	Acetonitrile	33600	42600 sh	44300 sh	45200 sh
	PVMI[b]	32800			
DHBI	Acetonitrile	33550[a]	42000	43000 sh	
	PVMI[b]	33100[a]	41600 sh		
3-*n*-Heptyl-2-PP	Acetonitrile	35200	43000—46000		
	PVMI[b]	34500			
3-*n*-Nonyl-2-PP	Hexane	35400[a]	42600 sh	43900 sh	45100 sh
	Acetonitrile	35500	42000—46000		
	PVMI[b]	34700			
3-Isopropyl-2-PP	Acetonitrile	35350	43000—46000		
	PVMI[b]	34300			
3-Methyl-2′,5′-dimethyl-2-PP	Hexane	36800	41600 sh	43100 sh	
	Acetonitrile	36800	40500—43500		
	PVMI[b]	36200	40000—42000		
3-Ethyl-2′.5′-dimethyl-2-PP	Hexane	36800	41600 sh	42900 sh	
	Acetonitrile	36800	40000—43500		
N-Ethoxyethyl-3-ethyl-2′,5′-dimethyl-2-PP	Hexane	36800	40000—42000		
	Acetonitrile	37300	39500—42000		
	PVMI[b]	36700	39000—42000		

[a] The fine structure of the band corresponding to the $S_0 \rightarrow S_1$ transition is manifested.
[b] Poly(vinyl-2-methylimidazole) matrix.

chromic shifts (3-methyl-2′,5′-dimethyl-2-PP, 1-ethoxyethyl-3-ethyl-2′,5′-dimethyl-2-PP). The introduction of an ethane bridge between the aryl and pyrrole moieties (also in positions 2′ and 3) causes an opposite shift. DHBI absorbs at even longer wavelengths than 2-PP. Thus, the spectroscopic effect of saturated substituents having similar electronic effects is determined by their positions in the molecules of 2-arylpyrroles. This fact can easily be explained by variation of the equilibrium torsion angle (φ_1) upon the introduction of a substituent or a bridge in positions 1, 3, and 2′. In fact, according to CNDO/S calculations (see Table 2), variation of φ_1 results in displacement of the longest-wavelength transition (λ_K) according to the equation ($0 \le \varphi_1 \le 75°$):

$$\lambda_K = (246\pm1) + (44\pm2)\cos\varphi_1,\ r = 0.997,\ n = 6.$$

Due to the inaccuracy of the semiempirical CNDO/S approximation, this equation cannot be directly used for the calculation of the φ_1 angle. In each particular case, its general form should be used, and the parameters should be found by calibration based on experimental results:

$$\lambda_K = \lambda_0 + \alpha\cos\varphi_1, \qquad (1)$$

where λ_0 is the wavelength of the absorption maximum for the conformation with $\varphi_1 = 90°$, and α is the slope (nm).

The short-wavelength absorption band of 2-arylpyrroles is caused, according to calculations, by a transition localized at the pyrrole moiety of the molecule ($S_0 \rightarrow S_3$). For most of 2-arylpyrroles, this band, unlike the band corresponding to the $S_0 \rightarrow S_1$ transition, has a resolved fine structure (see Fig. 2). The position and the shape of this band barely change upon the introduction of a methyl group in the aryl moiety. However, it is perturbed following the introduction of this group in the pyrrole moiety. When the size or the number of sub-

Table 2. Characteristics of the electronic absorption spectra of 2-PP and *N*-vinyl-2-PP found by CNDO/S calculations

φ^a/deg	$S_0 \to S_1$			$S_0 \to S_2$				$S_0 \to S_3$				
	λ/nm	f	$1\to1^{*b}$	λ/nm	$f\cdot10^2$	$1\to2^{*b}$	$2\to1^{*b}$	λ/nm	$f\cdot10$	$1\to3^{*b}$	$3\to1^{*b}$	$1\to4^{*b}$
						2-PP						
0	291	0.78	0.99	281	0.8	0.77	0.51	236	0.4	0.64	0.45	0.47
15	289	0.76	0.99	280	0.8	0.76	0.51	235.5	0.4	0.64	0.43	0.47
30	284	0.71	0.99	277	0.7	0.75	0.51	234.5	0.35	0.64	0.35	0.48
45	276	0.61	0.99	272	0.6	0.71	0.52	233.5	0.8	0.72	—	0.45
60	267	0.26^c	0.75^c	267.5	19^c	0.47^c	—	233	1.7	0.85	—	0.33
75	258.5	0.21	0.97	262	0.6	0.41	0.60	235.5	3.7	0.94	—	—
						N-Vinyl-2-PP[d]						
0	298	0.72	0.98	281.5	0.9	0.77	0.47	244.5	0.2	0.60	0.59^e	0.35^f
30	291	0.66	0.98	278	0.8	0.75	0.46	242.5	0.15	0.66	0.54^e	0.35^f
40	284.5	0.63	0.98	277	0.9	0.73	0.47	241.5	0.1	0.84	0.35^e	—
50	279	0.56	0.97	271.5	0.9	0.69	0.46	241.5	0.1	0.89	—	—
60	272.5	0.47	0.97	268	1.2	0.63	0.38	242.5	0.35	0.94	—	—
70	266.5	0.33	0.91	264	4.6	0.49	0.42^g	244.5	0.8	0.95	—	—
85	257	0.13	0.84^h	261	0.7	^{g}	0.35^g	250.5	2.6	0.85	^{h}	^{h}

[a] The dihedral angle between the aryl and pyrrole moieties. The angle of the deviation of the vinyl group from the plane of the pyrrole ring of *N*-vinyl-2-PP was taken to be 35°. A decrease in this angle by 15° results in a 2-nm shift of the longest-wavelength band to longer wavelengths. [b] The main configurations and coefficients of the expansion in terms of them. [c] Mixing of $1\to1^*$ and $1\to2^*$ configurations and borrowing of the intensities are observed. [d] 49 excited configurations were used in the calculations; in the case of 2-PP, the spectrum can be reproduced using only 25 configurations. [e] $4\to1^*$. [f] $1\to5^*$. [g] The $2\to3^*$ configuration is added. [h] The $1\to1^*$ and $1\to3^*$ configurations are mixed; the long-wavelength transition is degenerate into $1\to3^*$.

stituents in the five-membered ring increases (2-PP, 5-methyl-2-PP, 3-ethyl-2′,5′-dimethyl-2-PP, 3-*n*-nonyl-2-PP, and 1-ethoxyethyl-3-ethyl-2′,5′-dimethyl-2-PP), the band corresponding to the $S_0 \to S_3$ transition broadens, and its structure is smoothed (see Fig. 2, Table 1). This does not occur when substituents are introduced into the six-membered ring (*cf.* 3-ethyl-2′,5′-dimethyl-2-PP and 3-*n*-nonyl-2-PP, Fig. 2). Thus, experimental data completely confirm the assignment based on the calculations. Moreover, parameters of the fine structure of this band in the spectrum of 4′-methyl-2-PP are rather close to those of the long-wavelength absorption band of pyrrole, observed in a melt of this compound frozen to 77 K[22] (Table 3). In the case of 2-arylpyrroles, its energy almost coincides with that of the long-wavelength absorption of similarly substituted pyrroles. However, according to the multiconfiguration theory of second-order perturbations, long-wavelength transitions in pyrroles are degenerate.[23] Thus, Eq. (1) can be transformed in the following form:

$$\lambda_K = \lambda_P + \alpha\cos\varphi_1, \tag{2}$$

where λ_P corresponds to the experimental value of λ_0.

Table 3. Parameters of the fine structure of the band corresponding to a transition localized on the pyrrole moieties of molecules

Compound	ν*/cm^{-1}	ν$_1$/cm^{-1}				
4′-Methyl-2-PP	0^a	~700	1200	2100	3500	sh
Pyrrole[22]	0^b	520	~1210	2340	3360	3530

[a] ν_{exp} = 43300 cm^{-1}. [b] ν_{exp} = 44480 cm^{-1}.

***N*-Vinyl-2-arylpyrroles.** The introduction of a vinyl group in position 1 of alkylpyrroles leads to a shift of their long-wavelength absorption band (which corresponds to the $S_0 \to S_3$ transition) to 245—255 nm.[19] According to semiempirical calculations, the energy of the LUMO in *N*-vinylpyrroles changes, whereas that of the HOMO is retained, because the orbital electron density in position 1 is low. For the same reason, replacement of the hydrogen atom at the nitrogen atom in 2-arylpyrroles by a vinyl group should result in a red shift of the band in question. Theoretically (see

Table 4. Characteristics of π→π* transitions in the UV spectra (ν/cm^{-1}) of *N*-vinyl-2-arylpyrroles

Compound	Solvent	$S_0 \to S_1$	$S_0 \to S_3$
N-Vinyl-2-PP	Cyclohexane	37000	40300
	Acetonitrile	37500	40500 sh
N-Vinyl-DHBI	Hexane	32700^a	35600
	Acetonitrile	32800^a	35600
N-Vinyl-3-methyl-2-PP	Cyclohexane	37000	39400
	Acetonitrile	36800	39700
N-Vinyl-3-ethyl-2-PP	Cyclohexane	37200	39400
	Acetonitrile	37600	39700 sh
N-Vinyl-3-*n*-nonyl-2-PP	Hexane	37400	39600
	Acetonitrile	37700	39800
N-Vinyl-3-isopropyl-2-PP	Cyclohexane	37700	39700
	Acetonitrile	37900	39900
N-Vinyl-3-ethyl-2′,5′-dimethyl-2-PP	Hexane	38300 sh	39900
	Acetonitrile	38500 sh	40000

[a] The fine structure of the longest-wavelength band is manifested.

Table 2), if the conformation of the molecule is retained, the longest-wavelength band ($S_0 \rightarrow S_1$) should also undergo some bathochromic shift upon this substitution. In the real UV spectrum, the band corresponding to the $S_0 \rightarrow S_3$ transition in *N*-vinyl-2-arylpyrroles actually shifts to 250—260 nm (Table 4, Fig. 3). The bathochromic shift of the longest-wavelength band is observed only for bridged compounds, DHBI and *N*-vinyl-DHBI. For the rest of the pairs studied (2-PP and 1-vinyl-2-PP, 3-*n*-nonyl-2-PP and *N*-vinyl-3-*n*-nonyl-2-PP, 3-ethyl-2′,5′-dimethyl-2-PP and *N*-vinyl-3-ethyl-2′,5′-dimethyl-2-PP), this band undergoes hypsochromic shifts (see Tables 1 and 4). The replacement of the hydrogen atom in position 1 by a vinyl group is known[19] to cause a dramatic decrease in the dipole moments of heterocyclic molecules in the ground state. Provided that the dipole moment of the excited state is retained, this would result in a bathochromic shift of the observed bands. Formally, this does occur for the DHBI—*N*-vinyl-DHBI pair but not in other cases. All the above facts can be explained only by assuming that the equilibrium torsion angle between the aryl and pyrrole moieties increases substantially upon replacement of the hydrogen atom in position 1 by a vinyl group. Therefore, the position of the longest-wavelength band of *N*-vinyl derivatives of 2-arylpyrroles is determined by three factors: (1) the bathochromic solvatochrome shift resulting from the decrease in the dipole moment in the ground state; (2) the bathochromic shift caused by the replacement of the hydrogen atom in position 1 by the vinyl group; (3) the hypsochromic shift caused by an increase in the φ_1 angle. Whereas for *N*-vinyl-DHBI the two former factors predominate, for the rest of compounds the latter factor proves to be the crucial one, and, in addition, unbranched alkyl radicals in position 3 no longer have a significant effect on λ_K. Apparently, the introduction of the vinyl group sharply increases the φ_1 value; therefore, the steric strain created by nonbranched alkyl radicals is insufficient for its further increase. However, the introduction of an isopropyl group does cause a noticeable shift of the longest-wavelength band (see Table 4). The introduction of two methyl substituents in the phenyl fragment has a more pronounced effect (see Table 4). In the case of 3-ethyl-2′,5′-dimethyl-1-vinyl-2-PP, the longest wavelength band starts to coalesce with the band corresponding to the $S_0 \rightarrow S_3$ transition (see Fig. 3).

4,5-Dihydrobenzo[*g*]indole. Among 3-substituted 2-arylpyrroles, DHBI possesses the longest-wavelength absorption maximum. This band of DHBI, unlike those of other compounds, has a resolved structure, which is manifested not only in hexane but also in acetonitrile or in a polymeric matrix. Similar properties are characteristic of fluorene, whose molecule is known to be planar. In the case of 9,10-dihydrophenanthrene, a bridged compound, which is formally more similar to the compounds under consideration, and whose molecule, according to experimental data,[3] is non-planar ($\varphi_1 \approx 20°$), the long-wavelength band is structurized. According to published data,[15] DHBI exists in a planar conformation in the gas phase. This implies that in solution, the DHBI molecule is also planar.

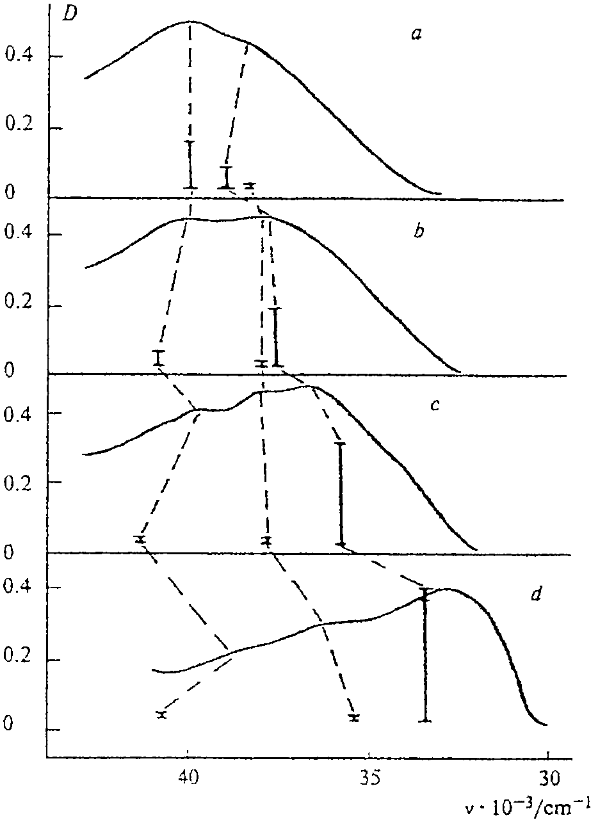
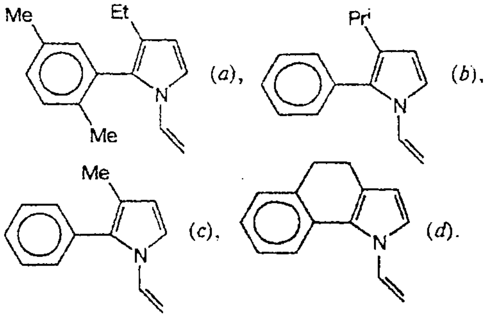


Fig. 3. Long-wavelength region of the UV spectra of solutions of *N*-vinyl-2-arylpyrroles in MeCN:



The vertical lines show the theoretical spectrum of *N*-vinyl-2-PP calculated for φ_1 = 85 (*a*), 70 (*b*), 50 (*c*), and 0° (*d*).

The effect of the solution—polymeric matrix phase transition. Absorption bands of DHBI in a polymeric matrix are displaced to longer wavelengths with respect to those in solution. The magnitude of this displacement (~3.5 nm) is typical of planar unsaturated molecules.[3] About the same shifts were found for polysubstituted

2-PP (3-methyl-2′,5′-dimethyl-2-PP and *N*-ethoxyethyl-3-ethyl-2′,5′-dimethyl-2-PP) which is apparently explained by their fairly "rigid" structures. In the UV spectra of 2-PP and its 4′- or 5-substituted derivatives, the shifts of absorption bands following the transition into a solid matrix are 2—3 times larger than the normal bathochromic shifts (see Table 1). This indicates that the molecules of 2-PP itself and of its 4′- and 5-substituted derivatives are non-planar in solution and that their geometries can change upon phase transition. However, it is impossible to predict the change in φ_1 based on the bathochromic shifts. In relation to 2-PP, which possesses a large bathochromic shift, this problem can be solved at a semiquantitative level using emission spectra. We chose DHBI as the model object. As had been expected, the shift of the fluorescence maximum of 2-PP observed on going from solution (338 nm, dioxane) to a crystalline sample (365 nm) was found to be too large (2200 cm^{-1}) compared to the shifts of fluorescence bands of planar molecules (1200 cm^{-1}).[24] The Stokes shifts of fluorescence bands of 2-arylpyrroles are presented below.

Compound	Medium	Stokes shift/cm^{-1}
DHBI	Dioxane	2900
2-PP	Dioxane	3150
2-PP	PVMI	2800

The Stokes shift of the fluorescence bands of 2-PP is much larger than that of DHBI in the same solvent.* Thus, the conclusion about the nonplanar structure of 2-PP in the liquid phase and its flattening in the solid phase is confirmed by the data of emission spectra. At the same time, the Stokes shift for 2-PP in a polymeric film coincides within ±100 cm^{-1} with the shift found for DHBI in dioxane. Thus, the molecule of 2-PP in a polymer film is planar.

***N*-Vinyl-4,5-dihydrobenzo[*g*]indole.** Among *N*-vinyl-2-arylpyrroles, *N*-vinyl-DHBI possesses the longest-wavelength absorption maximum. As in the case of DHBI, in the spectrum of *N*-vinyl-DHBI this band has a resolved structure, which is manifested both in hexane and in acetonitrile. On going from DHBI to *N*-vinyl-DHBI, the $S_0 \to S_1$ and $S_0 \to S_3$ transitions undergo bathochromic shifts, which are typical of compounds whose geometry does not change upon replacement of the hydrogen atom in position 1 by a vinyl group. The magnitude of the shift of the longest-wavelength band (10 nm) is approximately equal to that found by calculations (8 nm, see Tables 1, 2, and 4). The shift of the $S_0 \to S_3$ transition (~40 nm) is somewhat larger than that observed experimentally for alkylpyrroles upon replacement of the hydrogen atom in position 1 by a vinyl group (33 nm, on the average).[25] These data altogether make it possible to conclude that the molecule of *N*-vinyl-DHBI in solution is planar. In the gas phase, *N*-vinyl-DHBI exist in a non-planar conformation.[14]

Procedure for the calculation of equilibrium torsion angles from UV spectra. The information obtained makes it possible to formulate the following conditions for using Eq. (2) to estimate the φ_1 angles in 2-arylpyrroles in solution: (1) the slope α should be found using experimental values $\Delta\lambda = \lambda_K - \lambda_P$ for planar forms; (2) in the series of 3-alkyl-substituted 2-PP, it is better to take analytical values from the UV spectrum of DHBI in a specified solvent; (3) in the case of 4′- or 5-substituted 2-PP and unsubstituted 2-PP, Eq. (2) should be parametrized using the spectra obtained in a polymeric matrix and taking into account the bathochromic phase shift found for systems known to be planar; (4) for *N*-vinyl derivatives, the necessary values can be easily derived from the UV spectra of *N*-vinyl-DHBI in an appropriate solvent. The use of $\Delta\lambda$ values in the conformation analysis of 2-arylpyrroles makes it possible to counterbalance direct effects of substituents on individual electron transitions and thus to decrease the errors caused by different effects of electron correlation.

General characteristics of conformers of 2-arylpyrroles. Analysis of the UV spectra indicates that the molecules of 2-PP and 4′- and 5-substituted 2-PP in

Table 5. Torsion angles (φ_1) in 2-arylpyrroles and diphenyls in the gas phase[a]

Compound	φ_1/deg
DHBI	0
2-PP	30
4′-Methyl-2-PP	32
4′-Fluoro-2-PP	33
4′-Ethyl-2-PP	36±13
4′-Methoxy-2-PP	27±16
5-Methyl-2-PP	26
4′-Chloro-2-PP	34[b]
4′-Bromo-2-PP	40[b]
Diphenyl (DP)	41
4-Fluoro-DP	43
4,4′-Difluoro-DP	43
2-Fluoro-DP	47
2,2′-Difluoro-DP	62
4-Chloro-DP	49[b]
4,4′-Dichloro-DP	47[b]
4-Bromo-DP	54[b]
4,4′-Dibromo-DP	51[b]
3-*n*-Heptyl-2-PP	36
3-*n*-Nonyl-2-PP	32
N-Ethyl-4′-ethyl-5-hydroxyethyl-2-PP	57
N-Ethoxyethyl-2-PP	47
N-Vinyl-DHBI	20
N-Vinyl-2-PP	45
N-Vinyl-3-ethyl-2′,5′-dimethyl-2-PP	66
3-Methyl-2′,5′-dimethyl-2-PP	62
3-Ethyl-2′,5′-dimethyl-2-PP	63
N-Ethoxyethyl-3-ethyl-2′,5′-dimethyl-2-PP	64
N-Vinyl-3-methyl-2-PP	44±8
N-Vinyl-3-ethyl-2-PP	41
N-Vinyl-3-isopropyl-2-PP	47±7
N-Vinyl-3-*n*-nonyl-2-PP	39±10

[a] Found by a procedure described previously;[15] the error of determination of the angles was ±5. [b] See Ref. 16.

---

* Stokes shift was found as the difference between the wave number of the 0—0 transition and the center of gravity of the fluorescence band.

Table 6. Torsion angles (φ_1) in 2-arylpyrroles and diphenyls in solution

Compound	φ_1/deg
DHBI	0
2-PP	23±6
4′-Methyl-2-PP	23±6
4′-Fluoro-2-PP	23±9
4′-Chloro-2-PP	25±5
4′-Bromo-2-PP	26±5
5-Methyl-2-PP	22±9
N-Vinyl-2-PP	0
Diphenyl	23±9
4,4′-Dibromodiphenyl	28±9
3-*n*-Heptyl-2-PP	26±6
3-*n*-Nonyl-2-PP	29±4
3-Isopropyl-2-PP	29±7
N-Vinyl-2-PP	32±9
3-Methyl-2′,5′-dimethyl-2-PP	55±3
3-Ethyl-2′,5′-dimethyl-2-PP	53±3
N-Ethoxyethyl-3-ethyl-2′,5′-dimethyl-2-PP	64±3
N-Vinyl-3-methyl-2-PP	43±9
N-Vinyl-3-methyl-2-PP	53±3
N-Vinyl-3-*n*-nonyl-2-PP	53±3
N-Vinyl-3-isopropyl-2-PP	58±3
N-Vinyl-3-ethyl-2′,5′-dimethyl-2-PP	65±3

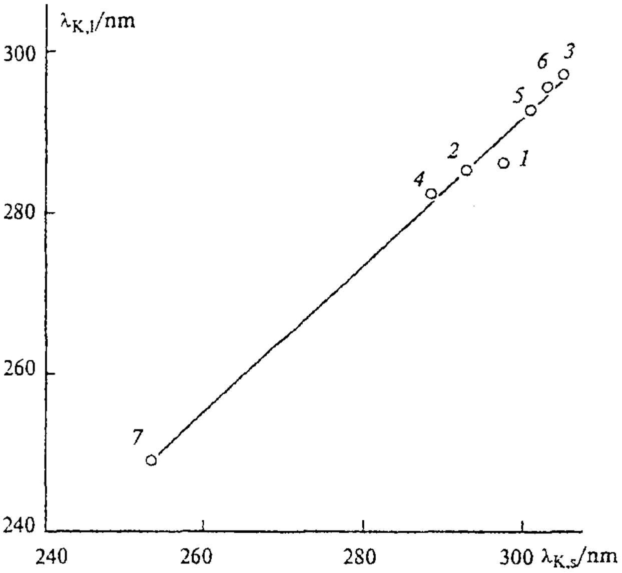


Fig. 4. Correlation of the position of the longest-wavelength maximum in acetonitrile ($\lambda_{K,l}$) and in the solid phase ($\lambda_{K,s}$): 2-PP (*1*), 4′-methyl-2-PP (*2*), 5-methyl-2-PP (*3*), 4′-fluoro-2-PP (*4*), 4′-chloro-2-PP (*5*), 4′-bromo-2-PP (*6*), diphenyl (*7*).

solutions are more planar than in the gas phase (Tables 5 and 6). The average decrease in the φ_1 angle in this series upon phase transition is 5°. Similar variations have also been observed for compounds with alkyl substituents in positions 3 or 3, 2′, and 5′. In the case of *N*-ethoxyethyl-3-ethyl-2′,5′-dimethyl-2-PP and 3-ethyl-2′,5′-dimethyl-1-vinyl-2-PP, the steric strain caused by substituents prove to be more significant than the effect of the medium. Therefore, their molecules are not flattened on passing to a solution. The torsion angles of 2-arylpyrroles in solution, as in the gas phase, depend on the number of substituents in positions 1, 3, and 2′ (see Tables 5 and 6). For unsubstituted compounds, the average angle in solution is 24°, for compounds with one substituent, it is 29°, for compounds with two substituents, this angle is 53°, and in the case of three substituents, it is 65°. To ascertain that the conclusion about flattening of alkyl-substituted 2-PP following the change in the physical state does not result from inadequate parametrization, we estimated the torsion angles in diphenyl. The parameters of Eq. (2) were determined from characteristics of the UV spectrum of ethylbenzene (λ = 208 nm), fluorene (λ = 261.5, 260.5, and 263 nm), and diphenyl (λ = 252, 251, and 253.5 nm) in hexane, acetonitrile, and a KCl matrix. The value of φ_1 found for diphenyl (see Table 6) permits the following conclusions to be made: (1) on passing from the gas phase to a solution, diphenyl flattens to a greater extent than alkyl-substituted 2-PP; (2) its equilibrium torsion angle is close to that for unsubstituted 2-PP and 4′- and 5-substituted 2-PP; (3) the resulting φ_1 value coincides with that obtained previously by a simpler method also based on UV spectra;[3] (4) the results agree qualitatively (the φ_1 angle in the liquid phase is smaller than in the gas phase) with those obtained by other methods, *viz.*, electrooptical method and IR and Raman spectroscopy (30—35°).[2]

The fact that the equilibrium torsion angles for the series of 2-arylpyrroles (2-PP, 4′-methyl-2-PP, 5-methyl-2-PP, 4′-fluoro-2-PP, 4′-chloro-2-PP, and 4′-bromo-2-PP) in solution are close to that for diphenyl permit an independent verification of this approach. If the φ_1 values of these compounds really do coincide, there should be a linear correlation (with a slope tangent other than unity) between the position of the longest-wavelength maximum in a particular solvent ($\lambda_{K,l}$) and its position in the solid phase ($\lambda_{K,s}$) in which φ_1 = 0°. This dependence actually holds (Fig. 4).

$$\lambda_{K,l} = (14\pm11) + (0.93\pm0.04)\,\lambda_{K,s},\ r = 0.996,\ n = 7.$$

As was expected, its slope (0.93) is close to the value cos(24°) = 0.91 ($\bar{\varphi}_1 \approx 24°$, see Table 6). The wavelengths for planar molecules obey a linear correlation with a slope tangent equal to unity (cos(0°) = 1.0). 3-Alkyl-substituted 2-PP in which the φ_1 angle in solution differs appreciably from 24° do not conform to these relations.

Thus, in the case of 2-arylpyrroles containing no substituents in positions 1, 3, and 2′, transition from the gas phase to a solution has a smaller effect on the conformation than the transition from a solution to a solid matrix in which the molecules become planar. Following the transition from the gas phase to the liquid phase, the equilibrium torsion angles of these molecules decrease by ~5°, whereas upon the liquid—solid transition, they decrease by ~25°. The effect of the physical state on the conformation of 2-arylpyrroles containing substituents in positions 2′, 3, and 5′ is much less pronounced. The conformations of compounds with three substituents in positions 1, 3, and 2′ do not change upon phase transitions.

The authors are grateful to V. I. Smirnov (Irkutsk Institute of Organic Chemistry of the Siberian Branch of the RAS) for assistance in the investigation of the emission spectra.

References

1. A. Almenningen, O. Bastiansen, L. Femholt, B. N. Cyvin, S. J. Cyvin, and S. Samdal, *J. Mol. Struct.*, 1985, **128**, 59.
2. A. Proutiere, D. Legoff, M. Chabanel, and E. Megnassan, *J. Mol. Struct.*, 1988, **178**, 49.
3. H. Suzuki, *Electronic Absorption Spectra and Geometry of Organic Molecules*, Academic Press, New York, 1967, 568 pp.
4. J. Trotter, *Acta Crystallogr.*, 1961, **14**, 1135.
5. C. P. Brock and R. P. Minton, *J. Am. Chem. Soc.*, 1989, **111**, 4586.
6. J. D. McKinney and P. Singh, *Acta Crystallogr.*, 1988, **C44**, 558.
7. A. Skancke, *Acta Chem. Scand.*, 1970, **24**, 1389.
8. L. Lunazzi, F. Salvetti, and C. A. Veracini, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1796.
9. G. J. Visser, G. J. Heeres, J. Wolters, and A. Vos, *Acta Crystallogr.*, 1968, **B24**, 467.
10. H. Lumbroso, D. M. Bertin, and F. Marschner, *J. Mol. Struct.*, 1988, **178**, 187.
11. A. V. Afonin, M. V. Sigalov, S. E. Korostova, S. A. Aliev, A. V. Vashchenko, and B. A. Trofimov, *Magn. Res. Chem.*, 1990, **28**, 580.
12. C. W. Fong, *Aust. J. Chem.*, 1980, **33**, 1763.
13. A. F. Ermikov, V. K. Turchaninov, K. B. Petrushenko, A. I. Vokin, S. E. Korostova, L. A. Ostroukhova, and Yu. L. Frolov, *Zh. Obshch. Khim.*, 1988, **58**, 450 [*J. Gen. Chem. USSR*, 1988, **58** (Engl. Transl.)].
14. V. K. Turchaninov, A. F. Ermikov, S. E. Korostova, and V. A. Shagun, *Zh. Obshch. Khim.*, 1989, **59**, 791 [*J. Gen. Chem. USSR*, 1989, **59** (Engl. Transl.)].
15. V. K. Turchaninov, A. I. Vokin, D.-S. D. Toryashinova, A. F. Ermikov, K. B. Petrushenko, and S. E. Korostova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 319 [*Russ. Chem. Bull.*, 1993, **42**, 275 (Engl. Transl.)].
16. V. K. Turchaninov, A. I. Vokin, D.-S. D. Toryashinova, S. E. Korostova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 869 [*Russ. Chem. Bull.*, 1993, **42**, 822 (Engl. Transl.)].
17. J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, 1968, **48**, 1807.
18. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 1975, **97**, 1285.
19. B. A. Trofimov and A. I. Mikhaleva, *N-Vinilpirroly* [*N-Vynilpyrroles*], Nauka, Novosibirsk, 1984, 262 pp. (in Russian).
20. B. A. Trofimov, in *Pyrroles. Part Two: The Synthesis, Reactivity, and Physical Properties of Substituted Pyrroles*, Ed. R. Alan Jones, J. Willey and Sons, New York, 1992, 131.
21. J. N. Murrell, *The Theory of the Electronic Spectra of Organic Molecules*, Academic Press, New York, London, 1964, 238 pp.
22. M. Bavia, F. Bertinelli, C. Taliani, and C. Zauli, *Mol. Phys.*, 1976, **31**, 479.
23. L. Serrano-Andres, M. Merchan, I. Nebot-Gil, B. O. Roos, and M. Fulscher, *J. Am. Chem. Soc.*, 1993, **115**, 6184.
24. J. O. Williams, *Chem. Phys. Lett.*, 1976, **42**, 171.
25. *Atlas spektrov aromaticheskikh i geterotsiklicheskikh soedinenii* [*Atlas of the Spectra of Aromatic and Heterocyclic Compounds*], Ed. V. A. Koptyug, Nauka, Novosibirsk, 1981, No. 21, 102 pp.

Received February 26, 1996;
in revised form March 28, 1997