Strong intramolecular hydrogen bond N—H...O in 2-(2-acyl-1-phenylethenyl)-5-phenylpyrroles

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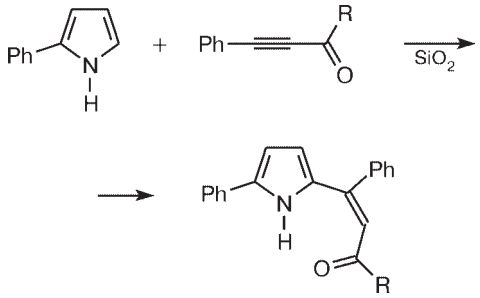
The molecular structure of 2-(2-benzoyl-1-phenylethenyl)-5-phenylpyrrole and 2-(2-furoyl-1-phenylethenyl)-5-phenylpyrrole was studied by X-ray diffraction analysis at 110 K and quantum chemistry methods (B3LYP/6-31G*). In the crystalline state, both compounds have cyclic structures closed by strong intramolecular hydrogen bond N—H...O. Canonic zwitterionic structure contributes largely to the ground state of the molecules. This is probably due to synergism of the H-bonding and π-electron interactions.

Key words: 2-(2-acylethenyl)-5-phenylpyrroles, intramolecular H-bond, X-ray diffraction analysis, nonempirical quantum-chemical calculations.

2-(2-Acyl-1-phenylethenyl)-5-phenylpyrroles are formed by the addition of 2-phenylpyrrole to 2-acyl-1-phenylacetylenes on silica exclusively in the form of *Z*-isomers[1,2] (Scheme 1).

Scheme 1



R = Ph, 2-furyl, 2-thienyl

The chemical shifts of the signals of the proton involved in the N—H bond, observed in the ^{1}H NMR spectra, and the stretching vibration frequencies of the NH and C=O groups in the IR spectra of these compounds are strongly different from those typical of the complexes with both intra- and intermolecular H-bonds between the amino and carbonyl groups.[3] One can assume that the intramolecular hydrogen bond (IHB) NH...O in 2-(2-acyl-1-phenylethenyl)-5-phenylpyrroles is strong and the nature of this bond should be studied in detail.

The intramolecular hydrogen bond in homonuclear systems was classified as strong.[4,5] This concerns both charged (—X—H...X$^-$—, =X...H$^+$...X=) and electrically neutral (—X—H...X=; X = O, N) systems in which the O or N atoms are involved in the conjugated double bond system. The heteronuclear fragment N—H...O is usually characterized by a weaker interaction. However, detailed analysis of the structural-chemical characteristics of heteronuclear systems showed that in some cases (if the formation of an H-bond is assisted by resonance[5—7]) rather strong IHB N—H...O can also be formed in these systems. Compounds with intramolecular resonance-assisted hydrogen bond (RAHB) are of great theoretical interest since they are promising for the development of molecular switch technology.[8—10]

In addition to the parameters of the ^{1}H NMR and IR spectra[5,7] the set of experimental criteria for the strength of an IHB also includes the length of this bond (the O...O or O...N distance), which is determined by X-ray or neutron diffraction analysis.[8,11—13] In the case of RAHB, variations of the O...O distance can span the range from 2.50 to 2.65 Å.[11] The N...O distance can vary over a broader range of values that are determined by the degree of delocalization of the π-electron density in the molecule and by the nature of substituents in its heterodiene fragments.

In this work, in order to determine the characteristics of the N—H...O bond, we carried out an X-ray diffraction study of single crystals of 2-(2-benzoyl-1-phenylethenyl)-

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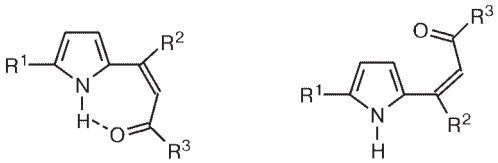
5-phenylpyrrole (**1**) and 2-(2-furoyl-1-phenylethenyl)-5-phenylpyrrole (**2**) and performed nonempirical quantum-chemical calculations of two rotamers of molecule **1**, one with (**1a**) and the other without (**1b**) the H-bond.



1a, **2a** **1b**

	R^1	R^2	R^3
1a	Ph	Ph	Ph
1b	Ph	Ph	Ph
2a	Ph	Ph	2-furyl

Results and Discussion

The results of the X-ray diffraction study and the calculated bond lengths, bond angles, and torsion angles in particular fragments of molecules **1** and **2** are listed in Tables 1 and 2, respectively, and the H-bond parameters are given in Table 3. The overall view of molecules **1** and **2** is presented in Fig. 1.

Table 1. Geometric parameters of the molecule of 2-(2-benzoyl-1-phenylethenyl)-5-phenylpyrrole (**1**) in the crystal and of its isomers **1a** and **1b**

Parameter	**1**[a]	**1a**[b]	**1a**[c]	**1b**[c]
Bond		*d*/Å		
O(1)—C(7)	1.247(2)	1.210	1.250	1.235
C(4)—C(5)	1.441(2)	1.451	1.434	1.446
C(5)—C(6)	1.372(2)	1.354	1.387	1.376
C(6)—C(7)	1.447(2)	1.470	1.451	1.463
N(1)—C(4)	1.379(2)	1.369	1.380	1.394
N(1)—C(1)	1.361(2)	1.345	1.358	1.366
C(1)—C(2)	1.394(2)	1.379	1.409	1.399
C(2)—C(3)	1.391(2)	1.402	1.395	1.401
C(3)—C(4)	1.398(2)	1.382	1.413	1.405
C(1)—C(14)	1.458(2)	1.473	1.463	1.462
C(5)—C(20)	1.496(2)	1.507	1.500	1.505
C(7)—C(8)	1.502(2)	1.504	1.505	1.511
Bond angle		ω/deg		
H(1)—O(1)—C(7)	—	118.2	114.6	—
H(1)—N(1)—C(4)	119.4(1)	122.1	119.5	123.7
N(1)—C(4)—C(5)	124.5(1)	125.7	124.2	119.8
C(4)—C(5)—C(6)	129.6(1)	131.2	129.6	129.9
C(5)—C(6)—C(7)	132.1(1)	131.2	132.2	131.1
O(1)—C(7)—C(6)	125.2(1)	125.1	125.9	124.6
Torsion angle		τ/deg		
C(6)—C(5)—C(4)—N(1)	−6.3(3)	0.1	−2.9	169.8
O(1)—C(7)—C(6)—C(5)	5.5(3)	−7.8	−1.7	0.0
C(6)—C(7)—C(8)—C(9)	23.6(2)	−27.4	−24.3	−22.7
N(1)—C(1)—C(14)—C(15)	−10.6(2)	−26.3	−6.5	−22.6
C(4)—C(5)—C(20)—C(21)	−54.2(2)	−72.8	−58.3	−60.4

Note. The atomic numbering scheme is identical with that used in Fig. 1.
[a] Experimental values.
[b] Obtained from HF/6-31G* calculations.
[c] Obtained from B3LYP/6-31G* calculations.

Table 2. Geometric parameters of the molecule of 2-(2-furoyl-1-phenylethenyl)-5-phenylpyrrole (**2**) for two independent molecules, **2′** and **2″**, obtained in the X-ray study

Parameter	**2′**	**2″**
Bond	*d*/Å	
O(1)—C(7)	1.249(2)	1.244(2)
C(4)—C(5)	1.435(2)	1.429(2)
C(5)—C(6)	1.374(2)	1.378(2)
C(6)—C(7)	1.443(2)	1.446(2)
N(1)—C(4)	1.375(2)	1.376(2)
N(1)—C(1)	1.358(2)	1.356(2)
C(1)—C(2)	1.398(2)	1.396(2)
C(2)—C(3)	1.393(2)	1.393(2)
C(3)—C(4)	1.401(2)	1.404(2)
C(1)—C(12)	1.464(2)	1.459(2)
C(5)—C(18)	1.497(2)	1.503(2)
C(7)—C(8)	1.472(2)	1.470(2)
Bond angle	ω/deg	
H(1)—N(1)—C(4)	119.7(1)	121.1(1)
N(1)—C(4)—C(5)	123.6(1)	123.4(1)
C(4)—C(5)—C(6)	129.2(1)	129.0(1)
C(5)—C(6)—C(7)	131.8(1)	131.9(1)
O(1)—C(7)—C(6)	127.3(1)	127.5(1)
Torsion angle	τ/deg	
C(6)—C(5)—C(4)—N(1)	0.5(2)	2.0(2)
O(1)—C(7)—C(6)—C(5)	−2.3(3)	2.0(3)
C(6)—C(7)—C(8)—O(2)	−3.7(2)	−3.8(2)
N(1)—C(1)—C(12)—C(13)	3.9(2)	−1.7(2)
C(4)—C(5)—C(18)—C(19)	−58.2(2)	60.2(2)

Note. The atomic numbering scheme is identical with that used in Fig. 1.

Table 3. H-Bond lengths (*d*) calculated by the HF/6-31G* and B3LYP/6-31G* methods for the molecules of 2-(2-benzoyl-1-phenylethenyl)-5-phenylpyrrole (**1**), its isomer **1a**, and 2-(2-furoyl-1-phenylethenyl)-5-phenylpyrrole (**2′**, **2″**)

Bond	*d*/Å				
	1[a]	**1a**[b]	**1a**[c]	**2′**[a]	**2″**[a]
N(1)—H(1)	0.99(2)	0.999	1.031	0.92(2)	0.92(2)
H(1)—O(1)	1.70(2)	1.815	1.673	1.74(2)	1.74(2)
N(1)—O(1)	2.620(2)	2.698	2.637	2.608(2)	2.604(2)
N(1)—H(1)—O(1)	153(2)	145.4	153.7	157(2)	155(2)

Note. The atomic numbering scheme is identical with that used in Fig. 1.
[a] Experimental values.
[b] Obtained from HF/6-31G* calculations.
[c] Obtained from B3LYP/6-31G* calculations.

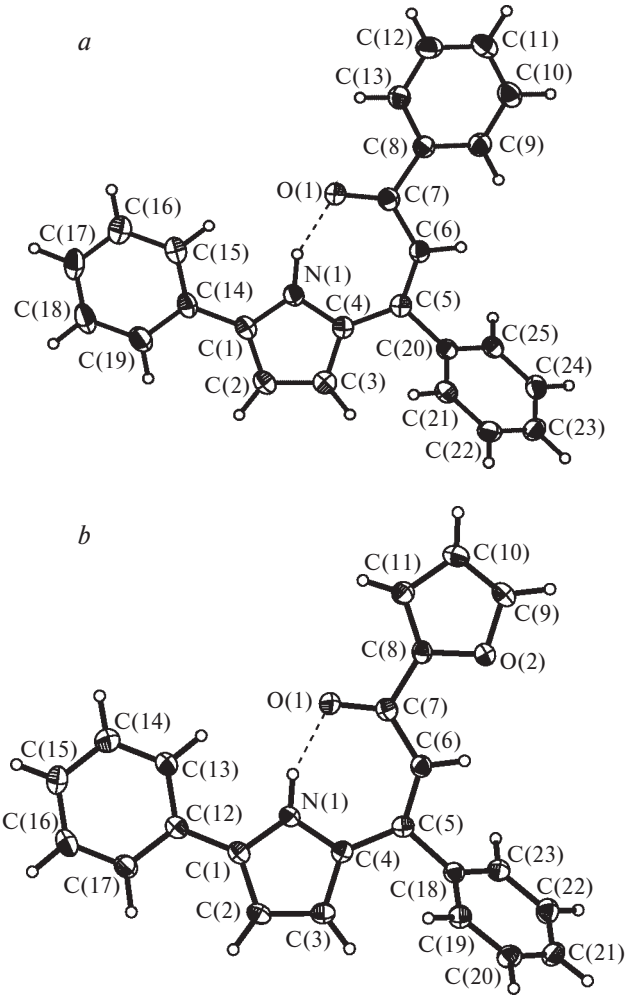
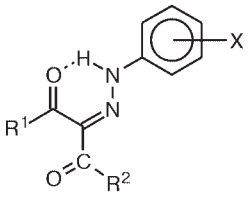


Fig. 1. Molecular structures of 2-(2-benzoyl-1-phenylethenyl)-5-phenylpyrrole (**1**) and 2-(2-furoyl-1-phenylethenyl)-5-phenylpyrrole (**2**). The non-hydrogen atoms are represented as probability ellipsoids (p = 50%) of anisotropic displacements.



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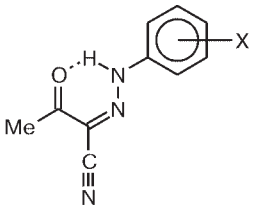


4

	R^1	R^2	X
3	Me	OMe	OMe, CN
4	—	—	Br, Me

In the crystal, both molecules represent *Z*-isomers with *s-cis* arrangement of the carbonyl group and olefinic C=C bond and have similar molecular packing. Two independent molecules, **2′** and **2″**, are also structurally similar. The bond angles and most of the chemically equivalent bonds of the 2-acylvinylpyrrole moiety of the structures in question are indistinguishable within the limits of experimental error. The phenyl and furyl substituents affect the N...O bond length (2.620(2) Å for $R^3 = C_6H_4$ and 2.608(2) Å for $R^3 = C_4H_4O$). For molecule **2**, this bond length approaches the upper bound of the range (2.54—2.61 Å) determined for compounds with RAHB, β-oxoarylhydrazones **3** and **4**.[12]

However, this feature cannot be used for unambiguous characterization of the nature of the hydrogen bond in these compounds. There are some additional arguments in favor of the high strength of the IHB in 2-acylvinylpyrroles. First of all, this is the fact that the N...O distances in the molecules of compounds **1** and **2** are strongly different from those in the molecules with "normal" IHB N...O with a length spanning the range from 2.9 to 3.2 Å[14] (in such molecules, either the donor or acceptor fragment is not involved in the entire π-system). The involvement of the N—H bond in the pyrroles **1** and **2** in strong intramolecular interaction is indirectly confirmed by the magnitudes of the spectral parameters of this bond, such as the chemical shifts, δ(NH), in the ^{1}H NMR spectra (δ 14.80 for **1** and 14.73 for **2**)[1] and the stretching vibration frequency (ν(NH) ~3000 cm^{-1} for **1**)[2] obtained for solutions of these compounds. These values virtually coincide with those found for α-oxo-α′-cyanohydrazones **4** (X = Br and Me, δ 14.87 and 14.97, respectively; ν(NH) = 3050 cm^{-1}).[12] By and large, the δ and ν(NH) values for β-arylketohydrazones[12] span the ranges from 12.70 to 15.47 for the former parameter and from 2950 to 3170 cm^{-1} for the latter. Thus, correlations between the structural and spectral characteristics of 2-acylvinylpyrroles **1** and **2** and β-oxoarylketohydrazones **3** and **4** point to a common formation mechanism of the RAHB and to synergism of the H-bonding and π-electron interactions.

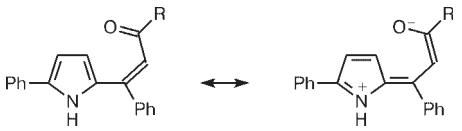
We carried out nonempirical quantum-chemical calculations of rotamers **1a** and **1b** of the *Z*-stereoisomer of molecule **1**. The geometric parameters of rotamer **1a** obtained from RHF/6-31G* calculations differ appreciably from the results of X-ray diffraction study. Reasonable agreement between theory and experiment can be obtained using calculations in the framework of the density functional approach with the B3LYP functional. This method allowed an adequate reproduction of the experimental results in calculations of the systems with RAHB.[12]

The results of the X-ray diffraction study of pyrroles **1** and **2** indicate that the C=O bonds in molecules **1** (1.244(2) Å) and **2** (1.244(2) and 1.249(2) Å) are longer than the interatomic distance in the carbonyl group in the —C=C—C=O fragment not involved in the IHB (1.208 Å).[15] The C=C bond is also lengthened from 1.325 to 1.372(2)—1.378(2) Å, whereas the =C—C= bond is shortened from 1.486 to 1.443(2)—1.447(2) Å. The observed changes of the geometric parameters of the seven-membered ring closed by the C=O...H—N hydrogen

bond can be explained by strong polarization of the π-system due to hydrogen bonding (a resonance of two canonic, a covalent and a zwitterionic, structures). Similar or even more pronounced changes in the double bond lengths occur as the size of the π-system increases (*cf.*, $l_{C=O}$ = 1.26 Å and $l_{C=C}$ = 1.38 Å for BrC_6H_4—CH=CH—CH=CH—$C(O)C_6H_5$ [16]); however, in this case the =C—C= bond in the —C=C—C=O fragment also remains long (1.48 Å). Equalization of the C=C, =C—C=, and C=O bond lengths in molecules **1** and **2** indicates a quasi-aromatic character of the π-system of the seven-membered ring.

Analysis of the geometric parameters of rotamers **1a** and **1b** revealed a similar trend in bond length variations (see Table 1). A salient feature of the geometry of these isomers should be pointed out. Calculations of rotamer **1b** showed that the C=C and C=O bonds remain rather long, while the =C—C= bond is relatively short (see Table 1), and that the π-system of the molecule is strongly polarized in the absence of IHB. Though equalization of the carbon—carbon bonds in molecule **1b** is less pronounced than in **1a**, the molecular structure can apparently be represented as a resonance hybrid with different contributions of the neutral and zwitterionic structures (Scheme 2):

Scheme 2

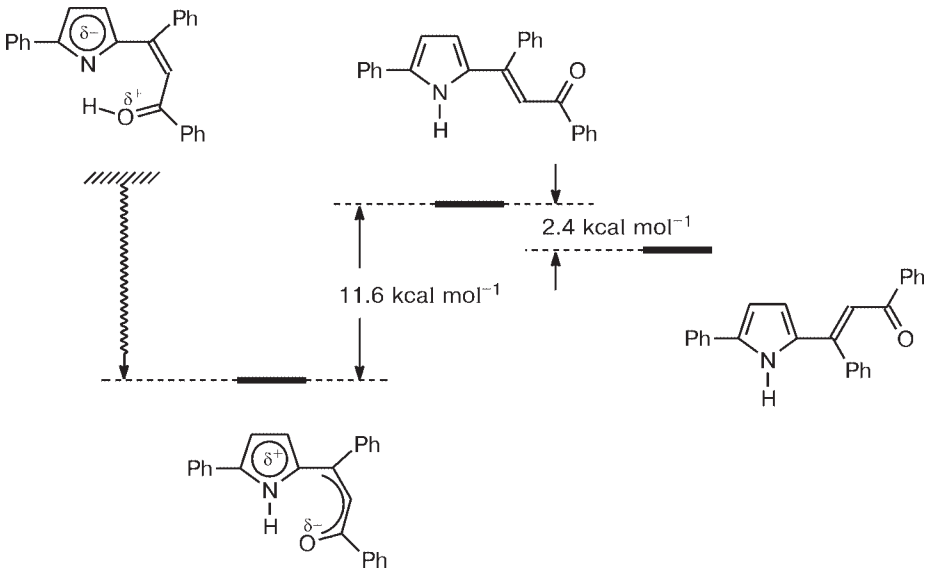


Our B3LYP/6-31G* calculations showed that, despite the strong polarization of the carbonyl group and N—H bond (the Mulliken atomic charges of C, O, N, and H are 0.400, –0.566, –0.758 and 0.419 e, respectively), rotamer **1a** is stable toward both tautomeric transformations of the molecules and their stereoisomeric (*Z*→*E*) transformation (Scheme 3). In Scheme 3, dashed lines denote the metastable state of the hydroxy form of the tautomer, which undergoes a spontaneous transition (denoted by a wavy arrow) into the equilibrium state. No local minimum corresponding to the hydroxy form of the tautomer represented as oxonium (by analogy with protonated acetone[17]) rather than carbonium cation was located on the potential energy surface in calculations of tautomeric transformations.

The contribution of the zwitterionic structure to the ground state of the molecule or system increases on going from conformer **1b** (the Mulliken atomic charges of C, O, N, and H are 0.394, –0.505, –0.718 and 0.339 e, respectively) to isomer **1a**, thus indicating a significant role of the IHB. Probably, synergism of the factors in question, *viz.*, the π-electron interactions in the seven-membered ring and the IHB, leads to high stability of conformer **1a**. The thermal effect corresponding to the formation of the IHB, estimated from the total energies of structures **1a** and **1b** taking into account the conformational isomerism, is ~10.0 kcal mol^{-1}. The conformational energy difference between **1a** and **1b** was set to the value found for two rotamers of the *E*-isomer (2.4 kcal mol^{-1}, see Scheme 3).

The results of our X-ray diffraction study and B3LYP/6-31G* calculations of geometric parameters of the *Z*-stereoisomer of compound **1** are in good agreement (see Table 1). This allows us to consider variations of the geometric parameters, due to the formation of the H-bond, using the calculated values only. In addition to

Scheme 3



the above-mentioned parameters, the C(4)—C(5)= and the N(1)—C(4) bonds in the pyrrole ring are affected to the greatest extent. The formation of the seven-membered ring leads to shortening of these bonds by 0.012 and 0.014 Å, respectively, as should be expected taking into account zwitterionic character of the ground state (see Scheme 2).

Thus, the results of our experiments and calculations indicate that strong intramolecular hydrogen bond is the main factor determining the molecular and electronic structure of 2-acylvinylpyrroles.

Experimental

The synthesis of compounds **1** and **2** was reported earlier.[1] The single crystals of compounds **1** and **2** used for the X-ray diffraction study were obtained by crystallization from EtOH (m.p. 149 °C) and by *in vacuo* sublimation at 3—5 Torr (m.p. 188 °C), respectively.

The results of our X-ray diffraction study and the refinement parameters are listed in Table 4. The experiments were carried out at 110 K and the temperature of the crystals was maintained using a low-temperature accessory (Oxford Cryosystem). The unit cell parameters and the crystal structure was determined with a Bruker SMART automatic diffractometer equipped with a CCD detector (50 kV, 35 mA, $\lambda(MoK\alpha) = 0.71073$ Å). The data collection covered a hemisphere of reciprocal space by a combination of four runs; each run was characterized by unique value of the angle φ (0, 90, 180, and 270°), an ω increment of 0.3°, and a 30 s exposure per frame. The distance between the crystal and detector was 3.933 cm. Completeness of the data collected was 100% for the angles up to $2\theta = 54°$. The integrated intensities of the independent reflections with inclusion of the Lorentz and polarization corrections were obtained using the SAINT program.[18] The absorption correction was included semiempirically (the SADABS program[19]).

Table 4. Principal crystallographic data and characteristics of the refinement of the crystal structure of compounds **1** and **2**

Parameter	**1**	**2**
Empirical formula	$C_{25}H_{19}NO$	$C_{23}H_{17}NO_2$
Molecular weight	349.41	339.38
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2(1)/c$
T/K	110(2)	110(2)
a/Å	7.7933(7)	18.912(3)
b/Å	19.4139(18)	6.1067(11)
c/Å	23.755(2)	29.277(5)
V/Å^3	3594.1(6)	3381.1(10)
Z	8	8
d_{calc}/g cm^{-3}	1.291	1.333
μ/mm^{-1}	0.078	0.085
F(000)	1472	1424
Crystal dimensions/mm^3	0.50×0.15×0.04	0.03×0.1×0.4
θ_{max}/deg	27.00	30.04
Number of measured reflections	22736	31830
Number of independent reflections	3910 ($R_{int} = 0.0572$)	9854 ($R_{int} = 0.0443$)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0435, 0.0933	0.0513, 0.1129
GOF	0.947	0.911

Quantum-chemical calculations of the molecules under study with full geometry optimization were carried out using the GAUSSIAN-98 program package.[21]

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