Conformation and Photoelectron Spectra of 2-(2-Furyl)pyrrole and 2-(2-Thienyl)pyrrole

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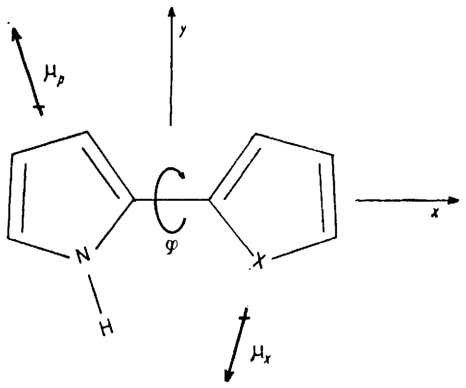
The electric dipole moments and He^I photoelectron spectra (p.e.s.) of 2-(2-furyl)pyrrole and 2-(2-thienyl)pyrrole have been measured and analysed. Dipole moment data, in conjunction with theoretical calculations of conformational energy at the *ab initio* STO–3G level, show that the most likely conformations for these molecules are the fully planar *cis* and *trans*, the former being more favourable. This conformational conclusion is supported by the p.e.s. evidence of strong mesomeric interaction between the two rings in both the molecules. Assignments of the p.e.s. bands have been made upon PMO analysis by comparison with those of the parent monocyclic compounds.

Elucidation of the molecular conformation and electronic structure of 2-heteroarylpyrroles is of fundamental importance since these compounds are precursors for the synthesis of chemotherapeutic compounds.[1] In this paper we present the results of an experimental and theoretical investigation on 2-(2-furyl)pyrrole (1) (Figure 1) and 2-(2-thienyl)pyrrole (2) (Figure 1). We have approached the conformational problem by an analysis of accurate electric dipole moment data obtained in benzene solution, which appear to be useful electronic parameters for structure–activity correlation studies, with the aid of quantum mechanical calculations at the *ab initio* level using the minimal STO-3G basis set.[2] This sort of calculation, which represents a reasonable compromise between the reliability of the results and the necessary amount of computational time, have been used successfully in a variety of conformational studies of substituted pentaheterocyclic compounds.[3] In order to clarify further the electronic structure and effects operating in these heterocyclic compounds we have measured and interpreted their photoelectron spectra (p.e.s.). P.e. measurements, in addition to their intrinsic interest, have also been performed with the aim of ascertaining whether some bands in the p.e. spectra could provide further conformational information on (1) and (2).



(1) X=O
(2) X=S

Figure 1 Molecular model of 2-(2-furyl)pyrrole (I) and 2-(2-thienyl)pyrrole (II) oriented along the reference axis system and direction of action of the component group moments. The *cis*-planar conformation (ϕ 0°) is shown

EXPERIMENTAL AND COMPUTATIONAL

Materials.—Samples of (1) and (2) were prepared and purified before use according to methods described previously.[4]

Physical Measurements.—The electric dipole moments of (1) and (2) were measured in benzene solution at 25 ± 0.1 °C using apparatus and techniques described elsewhere.[5] The total solute polarization was obtained by extrapolation to infinite dilution ($P_{2\infty}$) using the Halverstadt–Kumler method.[6] The value of the experimental molar refraction (R_D) for the Na$_D$ line was used as the electronic and atomic polarization ($P_e + P_a$) in calculating the dipole moment (μ) from Debye's formula. The μ values obtained (accuracy ±0.01 D) and the relevant polarization data are reported in Table 1.

Table 1

Polarization data and dipole moments
(in benzene at 25 °C)

Compound	α [a]	β [b]	$P_{2\infty}/\mathrm{cm}^3$	R_D/cm^3	μ/D
(1)	2.29	−0.288	91.15	40.2	1.58
(2)	2.76	−0.304	114.54	46.5	1.82

[a] $\alpha = \Sigma(\varepsilon_{12} - \varepsilon_{10})/\Sigma w_2$. [b] $\beta = \Sigma(v_{12} - v_{10})/\Sigma w_2$.

Gas-phase He^I p.e. spectra were measured with a Vacuum Generators UV G3 spectrometer[7] at elevated temperature [(1) at 40 and (2) at 80 °C] in the inlet system. Low resolution (30—50 meV; of full width at half maximum) for the complete spectra and high resolution (*ca.* 15 meV) with an expanded scale for individual systems were used. The energy scale was calibrated using the $^2P_{3/2}$ and $^2P_{1/2}$ lines of Xe and Ar. The p.e. spectra of (1) and (2) together with those of the parent monocyclic compounds pyrrole, furan, and thiophen are shown in Figure 2. The vertical ionization energies (I.E.s), defined for the highest peak in a system, are listed above the spectra; less certain values are given to one decimal place.

Computations.—*Ab initio* calculations were carried out with the Gaussian 70 program using the minimal STO-3G basis set.[8] Idealized structures of (1) and (2) were formed by connecting the actual geometries of furan, pyrrole, and thiophen [9] with a 1.47 Å bond. The total energies were computed for four conformations corresponding to dihedral angles ϕ between the planes of the rings of 0, 60, 120, and 180°. These energy values allowed the potential function $V(\phi)$ for internal rotation to be fitted by a truncated Fourier expansion (1), which, in turn, enabled the prediction of the

$$V(\phi) = \tfrac{1}{2}V_1(1 - \cos\phi) + \tfrac{1}{2}V_2(1 - \cos2\phi) + \tfrac{1}{2}V_3(1 - \cos3\phi) \quad (1)$$

minimum $V(\phi_{\text{min.}})$ and the maximum $V(\phi_{\text{max.}})$ in the potential function.

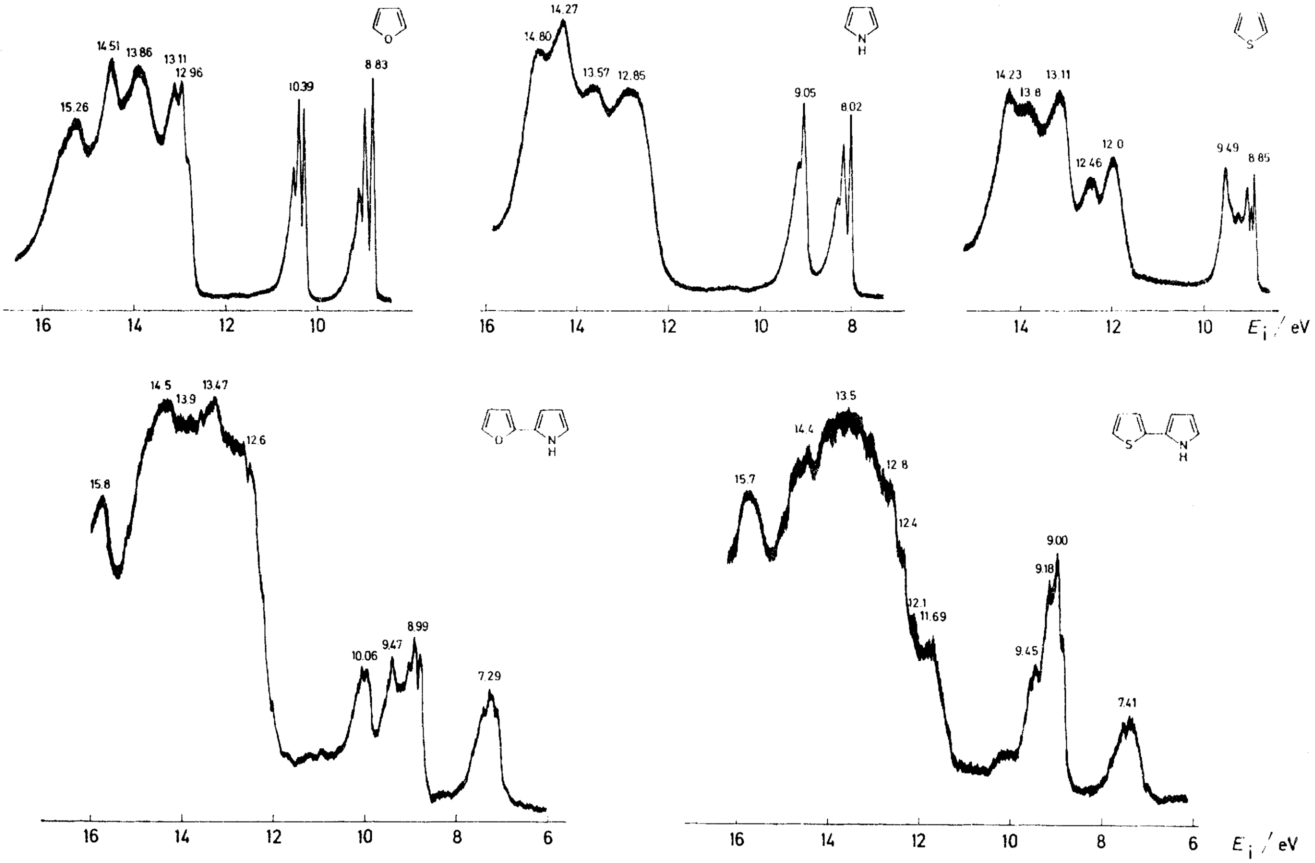


FIGURE 2 He^{I} Photoelectron spectra of furan, pyrrole, thiophen, 2-(2-furyl)pyrrole, and 2-(2-thienyl)pyrrole

RESULTS AND DISCUSSION

Conformational Analysis.—For (1) and (2) there are three possible situations which, in principle, can be expected: (i) free rotation, (ii) the existence of one single planar or twisted conformation, and (iii) an equilibrium between the NX-*cis*- and NX-*trans*-conformers. The conformational preference exhibited by these molecules is clearly governed by the relative importance of two factors, the π-interactions between the rings which tend to keep the molecules planar (the conjugative factor), and the non-bonding interactions which may be alleviated by deviation from planarity (the steric factor). Comparison between the experimental dipole moments (μ_{exp}) 1.58 D for (1) and 1.82 D for (2) (Table 1), and the theoretical values obtained for the three situations (i)—(iii) could provide essential information about the conformational problem. The theoretical dipole moments (μ_{calc}) of (1) and (2) have been therefore calculated as a function of the twisting angle ϕ by a three-dimensional vector addition method of group moments, using the group moments of furan (X = O; μ_X 0.72 D),[10] thiophen (X = S; μ_X 0.54 D),[11] and pyrrole (μ_P 1.81 D) [12] and the geometries specified above. The reference axis system and the direction of action of the group moments are shown in Figure 1 (the *cis*-planar conformation is assumed to have ϕ 0°).

If free rotation should occur, the calculated dipole moments of 1.95 D for (1) and 1.89 D for (2) would not be in good agreement with μ_{exp} especially in the case of (1). On the other hand, the hypothesis of two freely rotating rings is not very realistic due to the non-negligible energy barrier hindering this motion as demonstrated by the *ab initio* calculations (Table 2).

The dipole moments calculated for the *cis*- and *trans*-planar conformations are 1.47 D (*cis*) and 2.53 D (*trans*) for (1), and 1.44 D (*cis*) and 2.35 D (*trans*) for (2). For a model with a single planar conformation we find therefore that neither of the two planar *cis*- and *trans*-conformers matches the experimental data satisfactorily.

The μ_{exp} values could instead be accounted for quite well by advocating the existence of an equilibrium mixture of the two planar conformers and the preponderance of *cis* over *trans* in the ratios 92 : 8 for (1) and 64 : 36 for (2). This model could be reconciled easily with the results of the *ab initio* calculations, which predict the two planar conformations as the more favourable energetically for both (1) and (2) (Table 2).

TABLE 2

Calculated relative energies, potential constants, rotational barriers (in kcal mol^{-1}), and conformational angles for potential energy maxima

Molecule	Conformation	0°	60°	120°	180°
(1)	ΔE	0	3.97	4.23	1.01
(2)	ΔE	0	2.83	2.54	−0.74

	V_1	V_2	V_3	Barrier	$\phi_{max.}$ (°)
(1)	0.85	4.79	0.16	5.30	91.1
(2)	−0.69	4.08	−0.05	3.71	88.1

Finally, we have also tested the hypothesis that the molecules (1) and (2) adopt in the solution state a single twisted conformation. So far, the situation which holds for the condition $\mu_{exp} = \mu_{calc}$ occurs at ϕ 31° for (1) and at ϕ 73° for (2). This envisaged a tendency for (1) and (2) to assume a non-planar conformation in the solution state which can be qualitatively rationalized by invoking not only reaction field stabilization but also the conformational behaviour of similar molecules. In this regard it is meaningful to note that the related 2,2′-bithiophen molecule shows different conformations in different aggregation states, planar in the solid state,[13] twisted in non-polar solvents (dipole moment measurements),[11,14] and in the gaseous state,[15] and an equilibrium of two planar or nearly planar rotational isomers in e.s.r. experiments.[16] Taking into account, therefore, only the dipole moment data we hesitate to state with certainty that in the solution state the non-planar model is less likely than an equilibrium mixture of two planar conformers. Further conclusive information to overcome this dilemma is provided by a quantum mechanical treatment and the p.e. spectra.

The results of the *ab initio* calculations (Table 2) indicate that both (1) and (2) should assume, as isolated molecules in the gas phase, a planar conformation as the best compromise between opposing conjugation and steric factors.[*] In particular, the NO-*cis*-form is energetically favoured by 1 kcal mol^{-1} relative to the *trans* for (1) while the NS-*trans* by 0.74 kcal mol^{-1} relative to the *cis* for (2), the barriers of 5.30 and 3.71 kcal mol^{-1}, respectively, occurring near the 90° conformations. The most logical conclusion from these results is that an equilibrium between two planar conformers exists dominated by the more favourable one. Bearing in mind that the direction of the dipole moments of the furan and thiophen rings is the reverse of that of pyrrole, the simple picture in terms of dipolar interactions favours the *cis*-form for both (1) and (2). The STO-3G results are congruent with this expectation for (1) but not for (2). The theoretical preference for the *trans*-form of (2) is, however, certainly incorrect, being quite probably an artifact of the theory due to the erroneous dipole moment direction predicted by the STO-3G calculations for the thiophen ring. The primary theoretical result is, however, that the more stable conformer of both (1) and (2) (at least in the gas phase) is planar and less polar.

The expansion to a Fourier series of the potential function deserves some interest since it allows various physical effects on the mechanism of rotational barriers to be separated.[17] In particular, the physical effects reflected by the potential constants $V_i(\phi)$ for the present bicyclic compounds are, schematically, the interaction of local dipoles and steric hindrance (V_1), the tendency to adopt a uniplanar conformation in order to maximize conjugative stability (V_2), and the bond–bond repulsion (V_3). The results of Table 2 prove that the two-fold component (V_2) is most important and largely responsible for the rotational barrier. Furthermore, the V_1 component is more important than V_3 and, although smaller than V_2, plays a decisive role in assessing the relative stabilities of the *cis*- and *trans*-conformations. The energy barrier and the potential constant V_2 of (2) are smaller than those of (1), indicating less mesomeric interaction between the pyrrole and thiophen rings.

Photoelectron Spectra.—In order to assign the low-energy part of the p.e. spectra of (1) and (2) a qualitative perturbational molecular orbital (PMO) analysis [18] has been applied. The interacting fragments are pyrrole, furan, and thiophen whose π-orbitals, one a_2 and two b_1 characterised by standard HMO calculations,[19] yield in the p.e. spectra (Figure 2) systems at 8.02, 9.05, and 12.85 eV (pyrrole), and 8.83, 10.39, and 15.26 eV (furan), and at 8.85, 9.49, and 12.46 eV (thiophen).[20,†] Therefore, according to PMO analysis based upon these results, in the p.e. spectra of (1) and (2) four π-systems are expected in the low-energy region and two π-systems at somewhat higher I.E. accompanied by some σ ionizations. Moreover, a little destabilization of inductive origin or virtual constancy relative to the parent monocyclic compounds is anticipated for the uppermost π-MOs of b_1 origin while a sizeable splitting of the π-MOs of a_2 parentage due to inter-ring mesomeric interaction, which is larger in (1) than in (2), is shown by a previous Fourier analysis of the potential function.

Inspection of Figure 2 shows that the expectation is met. In particular, for (1) the six systems observed at 7.29, 8.99, 9.47, 10.06, 12.6, and 15.8 eV can be safely attributed to π-ionizations. The systems at 7.29 and 9.47 eV arise from the antibonding and bonding combinations of interacting furan and pyrrole a_2 orbitals,

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[*] For financial reasons the *ab initio* calculations did not take into account either possible changes of the inter-ring distance and of the NC(2)C(2′) and XC(2′)C(2) bond angles as a function of the twisting angle ϕ nor an AO basis set better than the minimal STO-3G. It may be that the profile of the potential function is somewhat influenced by these changes.

[†] The quoted assignment of the p.e. spectra of pyrrole and furan was established from intensity differences in their He^{I} and He^{II} p.e. spectra.[20] There are some differences in the assignments of the I.E.s relative to previous experimental studies and *ab initio* calculations.[21-25]

respectively (Figure 3). The second system at 8.99 eV corresponds mainly to the $\pi_2(b_1)$ orbital of pyrrole (Figure 3). In a first approximation, it cannot interact with the $\pi_2(b_1)$ orbital of furan, possessing one node at C(2) linking the furan and pyrrole rings. The lowest π-orbital of pyrrole may for symmetry reasons interact with the π_1 and π_2 orbitals of furan. Thus, the band at 12.6 eV in the p.e. spectrum of (1) appears at nearly the same energy as the $\pi_1(b_1)$ orbital of pyrrole, while systems at 10.06 and 15.8 eV arise from the antibonding and bonding combinations and are found at lower and higher I.E. than the $\pi_2(b_1)$ and $\pi_1(b_1)$ orbitals of furan, respectively.

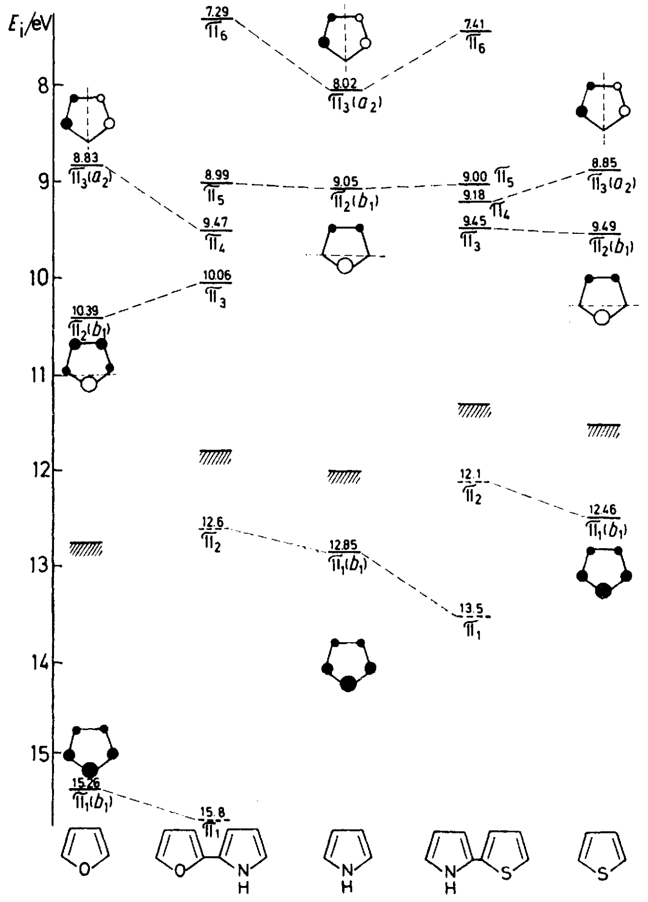

FIGURE 3 Partial correlation diagram of vertical ionization energies for furan, 2-(2-furyl)pyrrole, pyrrole, 2-(2-thienyl)-pyrrole, and thiophen

The systems at 7.29, 8.99, and 10.06 eV reveal vibrational structure: the corresponding vibrations may be characterized qualitatively by the assumption that their energy and nature are similar to those in the 2-substituted pyrroles and furans,[26] and that removal of a bonding electron would decrease the molecular vibration frequencies. Thus, the vibrational progression of 1 530 cm^{-1} observed in the band of the lowest I.E. can be correlated with the ν_4 carbon–carbon stretching mode of the 2-X-pyrrole nucleus. Both the systems at 8.99 and 10.06 eV show vibrational structure of *ca.* 950 cm^{-1}, which may be associated tentatively with the $\nu_{13}(\nu_{12})$ in-plane deformation mode of the 2-X-pyrrole nucleus and with the $\nu_{11}(\nu_{10})$ in-plane deformation mode of the 2-X-furan nucleus, respectively.

For (2) qualitative PMO analysis as for (1) gives four π-systems in the low-energy region of the p.e. spectrum, while the two high-energy π systems should be intermingled with σ ionizations. Therefore, by inspecting Figures 2 and 3, the six systems at 7.41, 9.00, 9.18, 9.45, 12.1, and 13.5 eV can be attributed to π-ionizations. In particular, the systems at 7.41 and 9.18 (9.45) eV correspond to antibonding and bonding combinations of pyrrole and thiophen a_2 orbitals, and the systems at 9.00 and 9.45 (9.18) eV are for symmetry reasons assigned to slightly inductively destabilized $\pi_2(b_1)$ orbitals mainly localized on pyrrole and thiophen rings, respectively. Finally, the two lowest π-systems at 12.1 and 13.5 eV arise from the antibonding and bonding combinations, respectively, of interacting pyrrole and thiophen $\pi_1(b_1)$ orbitals. The p.e. spectrum of (2) exhibits a resolved vibrational fine structure of 1 300 cm^{-1} in the system at 9.00 eV, which may be associated tentatively with the ν_7 ring stretching vibration of the 2-substituted pyrrole nucleus.

Assuming Koopmans' theorem to hold, a linear regression analysis based on the observed I.E.s and the *ab initio* STO-3G π-orbital energies ε_i calculated for the *cis*-conformers of (1) and (2),* $\mathrm{IE_i(eV)} = -0.710\,4\varepsilon_i + 3.540\,6$ (r 0.96), gives the orbital sequence, 7.46 (a_2, N), 9.05 (b_1, N), 9.45 (a_2, O), 9.90 (b_1, O), 13.53 (b_1, N), and 14.62 (b_1, O) eV for (1) which reproduces well the qualitatively derived ordering, and the sequence 7.36 (a_2, N), 8.82 (b_1, S), 9.05 (b_1, N), 9.37 (a_2, S), 12.43 (b_1, S), and 13.79 (b_1, N) eV for (2) with one inversion between π_3 and π_5 because of underestimation of the $\pi_2(b_1)$ orbital energy of the thiophen moiety.

Finally, it is to be stressed that the splitting (Δ) between the two I.E.s of a_2 parentage provides a measure of the mesomeric interaction between the two heterocyclic rings. Since the strength of this interaction is clearly related to the molecular conformation, being a maximum (and so Δ) in the fully planar arrangement and a minimum in the orthogonal conformation, one can regard Δ as a reliable index of deviation from planarity. Therefore, since the Δ value is 0.83 eV for the separated pair pyrrole–thiophen and increases to 1.8—2.0 eV for (2), this is diagnostic of a fairly strong π-interaction between the two rings and so of a clear preference of (2) for planarity. The alternative hypothesis of a single twisted conformation with a dihedral angle of 71° between the two rings, which is also compatible with the dipole moment data, can be thus ruled out. In the case also of (1) a similar observation, the Δ value changes from 0.81 eV of the separated pair pyrrole–furan to 2.18 eV in (1), yields a further strong argument in favour of the planar rather than the twisted conformation. It is worth noting that these conformational conclusions are fully

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* The theoretical results for the *trans*-conformers are only very slightly different from those of the *cis*.

consistent with the *ab initio* predictions for Δ, which varies as 2.0 eV (ϕ 0, 180°), 1.0 eV (ϕ 60, 120°), and 0.4 eV (ϕ 90°) in the case of (2) and shows a like behaviour also for (1).

In conclusion, the analysis of dipole moment data in conjunction with *ab initio* calculations of the conformational energies and with the p.e. evidence shows that (1) and (2) have a clear preference for a planar conformation, the NX-*cis*-form being more favourable than the NX-*trans*.

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