

Oxidation properties of β -substituted pyrroles

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Abstract Pyrroles represent building blocks of conjugated poly(heterocycles) which, as organic conductors, are potential materials for organic electronics. Oxidation of β -substituted pyrroles constitutes an important first step in the process of electropolymerization. Ionization energy and the electron spin density distribution are two the most important properties regarding monomers. These properties are studied as a function of electron-withdrawing and electron-donating substituents of pyrrole ring. Evolution of molecular structure, nature of bonding, and electronic density are studied as an effect of ionization process.

Keywords Conducting polymers · Substituted pyrrole · Ionization energy · Electron spin density

Introduction

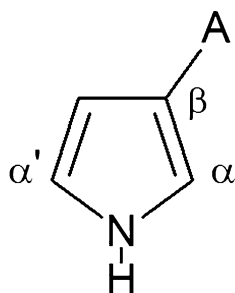
The conjugated poly(heterocycles), as potential organic conductors, are promising materials for application in the fast developing organic electronics [1]. The Nobel Prize in Chemistry, in 2000, for Heeger, MacDiarmid, and Shirikawa additionally amplified an interest in these materials.

Electropolymerization of pyrrole constitutes the milestone on the road of development of conducting polymers [2]. All proposed electropolymerization mechanisms indicate the oxidation of monomer as a first step [3]. Ionization constitutes the important parameter controlling the kinetics of polymerization and reactivity of fragments. Too high ionization energy leads to a number of side processes, and too small does not lead to the expected polymerization product [4]. Ionization activates the particular fragment of molecule, highly influencing further oligomerization reactions. Studies of oligomerization mechanisms indicate the extraordinary role of monomer cation, since polymerization process proceeds, almost exclusively, through the elongation of oligomer by the successive addition of the smallest building block [2, 3]. Redistribution of electronic density after the loss of electron controls the reactivity of polymerizing fragments. Both properties—ionization energy and electron spin density—may be controlled by the influence of aromatic properties of pyrrole ring. Since electropolymerization of five-membered heterocycles the most often proceeds through the carbon α position (Fig. 1), molecular properties may be controlled by the substitution in the β ring position. Systematic substitution of pyrrole by electron-withdrawing or electron-donating substituents has been studied regarding the influence on electron density properties of molecule with a special emphasis on the evolution of properties due to the loss of electron. Systematic studies may be useful for providing data for the controlled design of electropolymerization processes. Properties of monomers, as well as oligomers, may be significantly influenced by chemical substitution in the β position. The substituting groups, by donating or withdrawing electrons, influence the electron distribution within the heterocycle ring and, more importantly, activate carbon α and α' positions.

Dedicated to our friend Professor Oleg V. Shishkin from the STC “Institute for Single Crystals,” National Academy of Science of Ukraine.

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Fig. 1 Substituted pyrrole structure

sets including diffuse functions were also tested and found to have minor influence on studied properties. Atomic charges were computed using the natural bond orbital (NBO) [10] and Mulliken population analyses. The Gaussian 09 [11] suite of codes was used in all of these calculations. Representation of molecular structures and orbitals was prepared applying the GaussView 05 molecular graphics program [12].

Theoretical approach and computational details

Optimizations of studied structures were performed applying density functional theory (DFT) level of theory [5]. DFT approach utilizes the Becke's [6] three-parameter functional with the Vosko et al. [7] local correlation part and the Lee et al. [8] nonlocal part (abbreviated as B3LYP). No symmetry constraints were imposed during geometry optimizations. The standard cc-pVDZ basis set [9] was applied for the above optimizations. Extended basis

Results and discussion

Properties of pyrrole ring can be modified by substitution in β positions. The selected substituents represent different properties mostly related to possible charge transfer and conjugation with the ring. OH, NH₂, and NO₂ were selected for detailed presentation of properties and comparison with pyrrole. The pyrrole ring, due to nitrogen presence, possesses the C_{2v} symmetry. Substitution destroys the symmetry; however, pyrrole's molecular orbitals may still serve as a reference.

Table 1 Molecular structures, electron spin density (for cations), and three HOMO molecular orbitals (for molecules) representing π electrons for selected substituted pyrroles

Pyrrole	Pyrrole NO ₂	Pyrrole NH ₂	Pyrrole OH
Electron spin density			
HOMO			
HOMO-1			
HOMO-2			

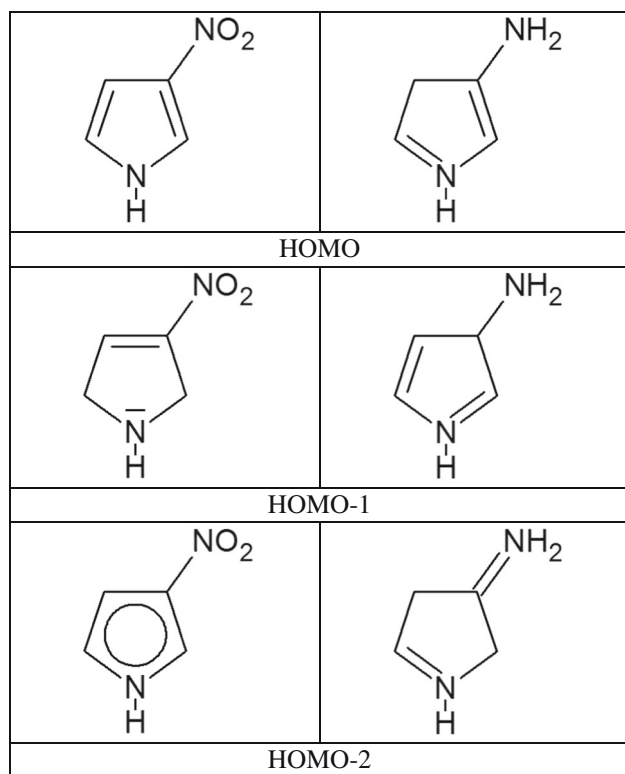


Fig. 2 Most important mesomers representing π -electrons for NO_2 (“withdrawing”) and NH_2 (“donating”) substituents

Molecular properties

NH_2 and NO_2 are known, in organic chemistry, as representatives of substituents donating and withdrawing electronic density from the aromatic ring. The molecular

Table 2 Important bond distances for selected substituted pyrroles and their corresponding cations (distances in Å)

Molecule			
Cation			

orbital representation of NO_2 derivative closely follows that of pyrrole (Table 1). The three HOMO orbitals, representing six aromatic electrons, are of the same topology. The MO picture indicates the weak conjugation of NO_2 with the ring. In the case of NH_2 , as well as all other electron-donating groups, the substituent is conjugated with the ring and symmetry is reduced to C_s . The schematic representation of mesomeric structures corresponding to molecular orbitals is shown in Fig. 2. The structure of rings in molecules is very similar (Table 2) regardless the substitution. Only the weak (~ 0.05 Å) elongation of $C(\beta)$ – $C(\beta')$ bond results from perturbations in the pyrrole ring aromatization. As expected, charge transfer from ring to the substituent group is the highest for the most electronegative acceptors (Table 3).

Cationic properties

Ionization of substituted pyrrole corresponds to the loss of electron from the HOMO orbital. The structure of molecular HOMO as well as structure of other occupied orbitals is to a large extent preserved. The picture of electron spin density corresponds closely to the one observed for molecular HOMO (Table 1). The unpaired electron of pyrrole and nitropyrrole cations is delocalized on the pyrrole ring. For other derivatives, delocalization is more extended and includes also the substituent.

Ionization leads to significant structure reorganization (Table 2). Pyrrole and nitropyrrole (representing electron-withdrawing group) cations possess the $C(\beta)$ – $C(\beta')$ double bond, while $C(\alpha)$ – $C(\beta)$ bonds are converted into single bonds. In case of NH_2 and OH derivatives (electron-

Table 3 Atomic charges from NBO and Mulliken (in parentheses) population analysis in molecules and cations and corresponding electron spin densities (in electrons) and vertical and adiabatic ionization energies (in eV) for studied pyrrole derivatives

Derivatives	Pyrrole-H	–NO ₂	–NH ₂	–OH	–Br	–Cl	–F	C ₃ H ₇	–OCH ₃
Molecule atomic charge									
A	0.230 (–0.041)	–0.284 (–0.362)	–0.073 (0.014)	–0.226 (–0.054)	0.064 (–0.076)	–0.008 (–0.109)	–0.346 (–0.164)	–0.023 (0.051)	–0.413 (–0.085)
α	–0.050 (0.047)	–0.008 (0.103)	–0.118 (0.036)	–0.156 (0.008)	–0.051 (0.101)	–0.058 (0.111)	–0.132 (0.030)	–0.056 (0.010)	–0.156 (–0.006)
α'	–0.050 (0.047)	–0.033 (0.079)	–0.033 (0.061)	–0.031 (0.063)	–0.033 (0.062)	–0.032 (0.062)	–0.032 (0.062)	–0.040 (0.062)	–0.031 (0.068)
N	–0.574 (–0.042)	–0.557 (–0.034)	–0.574 (–0.042)	–0.573 (–0.044)	–0.566 (–0.042)	–0.567 (–0.042)	–0.570 (–0.043)	–0.573 (–0.045)	–0.573 (–0.049)
Cation atomic charge									
A	0.286 (0.069)	–0.118 (–0.172)	0.229 (0.329)	–0.040 (0.166)	0.368 (0.248)	0.237 (0.157)	–0.249 (–0.024)	0.136 (0.294)	0.005 (0.197)
α	0.229 (0.220)	0.238 (0.252)	0.096 (0.184)	0.103 (0.167)	0.193 (0.250)	0.199 (0.264)	0.160 (0.192)	0.218 (0.197)	0.082 (0.138)
α'	0.229 (0.229)	0.237 (0.228)	0.071 (0.146)	0.112 (0.161)	0.147 (0.169)	0.160 (0.175)	0.185 (0.189)	0.183 (0.189)	0.086 (0.153)
N	–0.592 (–0.022)	–0.578 (–0.017)	–0.542 (–0.018)	–0.548 (–0.018)	–0.560 (–0.018)	–0.563 (–0.018)	–0.572 (–0.021)	–0.582 (–0.027)	–0.541 (–0.021)
Atomic electron spin density									
A	–0.003 (–0.004)	0.021 (0.019)	0.314 (0.311)	0.172 (0.168)	0.196 (0.186)	0.148 (0.140)	0.064 (0.060)	0.035 (0.032)	0.217 (0.215)
α	0.494 (0.517)	0.463 (0.481)	0.375 (0.385)	0.408 (0.421)	0.392 (0.408)	0.415 (0.431)	0.467 (0.485)	0.468 (0.483)	0.384 (0.396)
α'	0.494 (0.517)	0.494 (0.514)	0.125 (0.133)	0.234 (0.249)	0.336 (0.354)	0.360 (0.380)	0.404 (0.427)	0.422 (0.444)	0.180 (0.191)
N	–0.086 (–0.100)	–0.089 (–0.102)	0.077 (0.074)	0.052 (0.048)	–0.021 (–0.029)	–0.026 (–0.035)	–0.035 (–0.044)	–0.045 (–0.056)	0.077 (0.073)
IE _{ver}	8.111	9.042	7.166	7.662	8.106	8.199	8.277	7.757	7.542
IE _{ad}	7.938	8.835	6.655	7.391	7.922	7.991	8.038	7.571	7.237

donating group), the bond C(β)–C(β') remains unchanged (single), while new double bond is formed between N and C(α). Interestingly, this picture corresponds to the schematic representation of HOMO-1 molecular orbital (Fig. 2).

The loss of electron influences the electron density distribution. The picture, however, closely follows the symmetry of molecular HOMO orbitals (Table 1). The schematic picture for atomic charge redistribution (Fig. 3) indicates the highest activity on α carbon sites. Similarly, electron spin density indicates the highest reactivity α (or α') carbon sites. In pyrrole amine, charge effect is similar, although smaller. Additionally, significant positive charge is observed on the NH₂ group, indicating its conjugation with a pyrrole ring. The electron spin density, however, is distributed between C(α) and NH₂ sites, while the C(α') center is much less “radical.” The above observations

represent general finding and divide derivatives into two groups with respect to response to an ionization phenomenon. The nitrogen center inside the ring is only weakly affected by ionization.

Influence of β substitution, visible on electronic properties, significantly influences stability of molecules. Vertical ionization energy, taken as a measure of electron density delocalization in a molecule, indicates the highest stabilization of nitropyrrole (9.04 eV). On the other side, the strongest electron-donating substituent—fluorine—leads to the highest stabilization in this group. Some observed perturbations within the relation between vertical ionization energy and charge and spin distributions indicate the competing influence of electronic factors on energetic parameters. The high difference between vertical and adiabatic ionization energies confirms high changes in structure and nature of bonding due to the loss of electron.

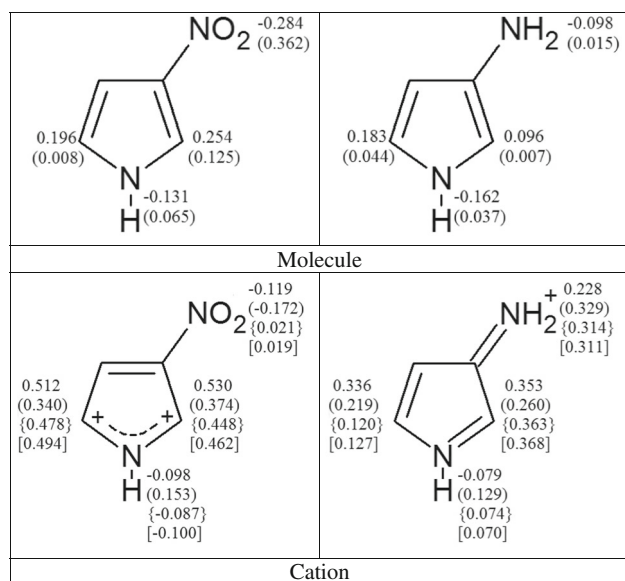


Fig. 3 NBO and Mulliken (*in parentheses*) atomic charges on selected atoms with hydrogens summed into it, for NO₂ and NH₂ pyrrole derivatives. The NBO and Mulliken atomic electron spin densities (*in parentheses* and *square brackets*, respectively) are additionally given for cations. Values in electrons

Conclusions

Ionization energy of monomers and electron density distribution constitute two of the most important factors for the electropolymerization process of conjugated heterocycles. Substitution of aromatic rings provides the way to control microscopic properties. Substitution of pyrrole allows for wide selection of values of properties of interest. The “withdrawing” and “donating” substituents lead to different organization of electron density as well as bonding structure in derivatives. Ionization process leads to significant structural changes which, more importantly, are qualitatively different regarding the nature of substituents. The possible conjugations of six π electrons in aromatic pyrrole ring lead to two possible patterns. In both cases, C(α) is activated by the localized radical electron. The model cases nitropyrrrole and pyrrole amine additionally possess unpaired electrons on C(α') for nitro and on NH₂ for amino derivative. Population analysis indicates the differences in atomic charge distribution and electron spin density pictures. Ionization energy, to a large extent, is controlled by the nature of substituting group. The

deconjugation process due to the loss of electron leads to the significant changes in pyrrole’s skeleton, leading to the large differences between vertical and adiabatic properties.

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