



Theoretical study of structure and electronic properties of cyano-substituted pyrroles

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ABSTRACT

DFT and *ab initio* MP2 calculations of optimal geometries, dipole moments, polarizabilities, excitation energies and enthalpies of hydrogen or proton transfer from N–H group for cyano derivatives of pyrrole are presented. CN groups in α and β positions have distinct effects on electron spectra absorption bands. CN in α position causes larger bathochromic shift in comparison to β position. N–H bond dissociation enthalpies (BDE) of substituted pyrroles are higher by 7 kJ mol^{-1} than pyrrole BDE. Number and position of CN groups do not affect BDEs. Proton affinities of pyrrolyl anions and enthalpies of electron transfer from these anions are proportional to the number of CN groups in molecule. Each CN group causes decrease in proton affinity by 72 kJ mol^{-1} and 73 kJ mol^{-1} rise in electron transfer enthalpy. For several studied pyrroles, BDEs, proton affinities and electron transfer enthalpies in water and benzene were computed.

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1. Introduction

Compounds based on the pyrrole aromatic ring are ubiquitous in nature. Due to its role as a structural building unit in many biologically important molecules and the relevance of pyrrole and its derivatives in the syntheses of biologically active compounds, photosensitizers for photodynamic therapy, conducting organic polymers, pesticides and organometallic magnetic compounds or materials for optoelectronic industry, considerable effort has been focused on the understanding of pyrrole electronic structure and photochemical properties [1–7]. Moreover, pyrroles and other nitrogen-containing heterocyclic compounds serve as the main source of fuel nitrogen in coals and heavy-oils [8,9].

In the last decade, extensive experimental and theoretical studies have been performed to elucidate spectroscopic properties and the thermochemistry of five-membered nitrogen-containing heterocycles [2–17]. Knowledge of the N–H bond dissociation enthalpies (BDEs) and proton affinities (PAs) of pyrrolyl anions, of pyrrole and substituted pyrroles is of value for energetic considerations and for the construction of mechanisms to model their combustion or oxidation processes [10,11,18]. It is also known that conducting polymers such as polypyrrole and its derivatives do not possess good stability in the presence of oxygen and water [19].

The relative low stabilities and highly exothermic combustion or oxidation of nitrogen-containing heterocyclic compounds cause

difficulties in experimental study of their thermochemistry. Therefore, quantum chemical calculations represent a valuable tool for this kind of studies. Barckholtz et al. [10] employed several computational methods, including HF, MP2 and DFT, for C–H and N–H BDE calculations of small aromatic hydrocarbons. They found that HF and MP2 methods are not able to adequately describe both the parent molecule and the radical resulting from hydrogen atom loss. The two methods also suffered from significant spin contaminations. In the work [20], the authors found that MP2, MP3 and MP4 methods did not provide reliable phenolic O–H bond dissociation enthalpies for *ortho*-, *meta*- and *para*-substituted phenols. Moreover, these methods were unable to describe substituent effect on BDE correctly. da Silva et al. [11] employed the CBS-APNO, G3 and G3B3 theoretical methods to obtain N–H and C–H BDEs of various five-membered nitrogen-containing heterocycles.

Substitutions (derivatization of the monomer structure) represent one of the main strategies employed for modification of properties of compounds or polymers [19]. In organic synthesis, cyano groups play a very special role. Strong electron-withdrawing CN groups incorporated into the aromatic monomer units, designed for the preparation of conductive oligomers or polymers, induce the reduction of the barrier for electron injection, the increase in the oxidation potential [21] and improvement of the electron-transporting properties. Besides, the CN group can perturb the π -conjugation, leading to significant changes in the strength of adjacent bonds. Cyano-substitution in aromatic amines, phenols and thiophenols alters the reaction enthalpies of many important processes, e.g. hydrogen atom transfer (see Scheme 1), representing

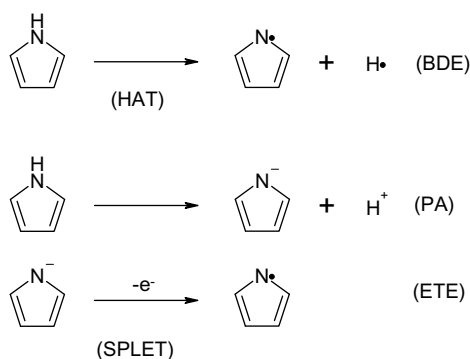
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the first step of primary antioxidants action, or proton affinity of the corresponding anion [22,23]. The investigation of CN group effects on the pyrrole is therefore able to help us to understand and predict the behavior and physico-chemical properties or oxidative stability of pyrrole derivatives or larger oligomeric and polymeric systems [24]. Moreover, polymers are not more susceptible to oxidation than their low-molecular-weight counterparts [25].

In this work, we will focus the attention on the quantum chemical calculation of pyrrole and nine cyano-substituted pyrroles (Fig. 1). These compounds have not been systematically studied in order to describe the effect of CN substitutions on the pyrrole geometry, permanent dipole moment, polarizability, vertical excitation energy or the gas- and solution-phase energetics of (H^\bullet) or H^+ abstraction from N–H bond yet. We have employed DFT (Density functional theory) and *ab initio* MP2 (Møller–Plesset perturbation theory up to the second-order) methods for the calculation of optimized electronic ground-state geometries, dipole moments and electric polarizabilities. In this study, PBE0 functional was chosen, because it was reported that the functional is able to provide dipole moments and polarizabilities [26], proton affinities [27] and vertical excitation energies [28] of various small and medium-size molecules or radicals in good agreement with experimental data and more computationally demanding methods. In the case of MP2 method, we have chosen frozen-core approach, since it represents a reasonable compromise between the accuracy of the results and computational costs. We have performed all-electron MP2 calculations for pyrrole and several CN-substituted pyrroles. Differences in the computed quantities (bond lengths, dipole moments and polarizabilities) were smaller than 0.2%.

For the obtained optimal geometries, vertical excitations have been calculated using several quantum chemical methods based on time dependent TD-DFT theory. N–H bond dissociation enthalpies related to the hydrogen atom transfer (HAT) mechanism, proton affinities and electron transfer enthalpies (ETEs), related to the sequential proton loss electron transfer (SPLET) mechanism [23,29] (Scheme 1), have been calculated using DFT method. In addition, all computed characteristics will be compared with available experimental data. Finally, the role of the number of CN groups



Scheme 1. Reaction schemes for hydrogen atom transfer and sequential proton loss electron transfer mechanisms and denotation of the corresponding reaction enthalpies for pyrrole and its derivatives.

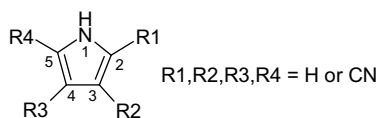


Fig. 1. Atom numbering and denotation of pyrroles under study. In the text and tables, **P** represents non-substituted pyrrole, **P4CN** tetracyano-substituted pyrrole. Denotation of the rest of studied molecules reflects the positions of the CN groups on the ring.

in all possible positions in the pyrrole molecule will be analyzed and discussed.

2. Methods and calculation details

Full geometry optimizations were carried out at the DFT (PBE0 functional) and *ab initio* frozen-core MP2 levels of theory (energy cut-off of 10^{-5} hartree mol^{-1} , final RMS energy gradient below 2×10^{-5} hartree $\text{mol}^{-1} \text{Å}^{-1}$). Total enthalpies of each studied neutral, radical, and anion molecule were obtained using the PBE0 approach at $T = 298.15$ K. The polarized triple-zeta valence TZVP [30] basis set has been used for the geometry optimization. On the basis of optimized geometries, the electronic absorption spectra, permanent dipole moments and polarizabilities were calculated. Vertical excitations were computed using the TD-PBE0 method for PBE0/TZVP geometries. Electric properties and excitation energies were calculated using the TZVP basis set augmented by a set of diffuse functions whose exponents have been obtained from the lowest s, p and d exponents by division of a factor of 3 (denoted as TZVP+) [31]. All calculations (MP2, DFT and TD-DFT) were performed using Gaussian 03 [32].

When a molecule is placed in an external electrostatic field characterized by vector \vec{E} molecular charge reorganization causes a dipole moment change according to Eq. (1) [33]:

$$\vec{\mu} = \vec{\mu}_0 + \vec{\alpha} \cdot \vec{E} + \dots \quad (1)$$

where $\vec{\mu}_0$ is the permanent dipole moment. The property $\vec{\alpha}$ is a second rank tensor called the first-order polarizability. The components α_{ii} ($i = x, y, z$) of the diagonalized tensor and the associated properties, i.e. the averaged polarizability α_{ave}

$$\alpha_{\text{ave}} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

and the anisotropic polarizability $\Delta\alpha$

$$\Delta\alpha = \sqrt{\frac{1}{2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2]} \quad (3)$$

are quantities of great interest in optoelectronics and intermolecular forces. Static values of first-order polarizabilities were evaluated analytically employing the Finite-Field theory. Electron correlation contributions to the permanent dipole moments, μ_0 and polarizabilities, α were computed at the MP2/TZVP+ and PBE0/TZVP+ levels of theory. Studied molecules were oriented in y - z plane. Therefore, α_{xx} polarizability component is perpendicular to the plane of the pyrrole ring.

3. Results and discussion

3.1. Optimal geometries

In the case of all studied pyrroles, DFT and MP2 geometry optimizations provided planar structure of the molecules. Obtained theoretical bond lengths are compiled in Table 1. In the case of pyrrole **P**, DFT and MP2 methods indicate the maximum bond length between C_3 and C_4 atoms, while the distances between the N_1 and C_2 (C_5) atoms of the ring are the shortest. In comparison with experimental data [35], the PBE0/TZVP approach gives longer bonds, while MP2/TZVP results are in better accordance to experimental bond lengths. Differences between experimental and MP2/TZVP bond lengths are within 0.002 Å, with the exception of N_1 -H bond lengths, where MP2/TZVP provides bond longer by 0.011 Å. On the other hand, HF/6-31G** method [34] provided shorter bond lengths in comparison with experiment. Substituents lead to the structural perturbation dependent on the mutual position of the CN groups on the aromatic ring. Generally, if α substitution domi-

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