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Predicting molecular properties using theoretical parameters: substituted pyridines

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The potential of three alternative theoretical quantities – NBO atomic charges, Hirshfeld charges, and electrostatic potential at nuclei (EPN) values – in predicting molecular properties is examined for a series of 37 substituted pyridines. These molecular parameters were evaluated using density functional theory computations at ωB97X-D/aug-cc-pVTZ. Correlations with experimental basicities (pK_b) and proton affinities (PA) as well as with theoretically estimated hydrogen bonding energies (for complexes with HF and H_2O) show that the EPN values at the pyridine nitrogen (V_N) provide the best predictive power among the considered theoretical parameters.

Keywords: pyridines, atomic charges, electrostatic potential at nuclei, Density functional theory, hydrogen bonding.

INTRODUCTION

In this research, we examine the potential application of theoretical molecular parameters in predicting the reactivity of 3- and 4-substituted pyridines with respect of hydrogen bonding and in characterizing their proton affinities and basicities. Quantifying chemical reactivity has been in the focus of theoretical studies for decades. Important developments on this respect represent the methods employing the properties of the frontier orbitals, first considered quantitatively by Fukui [1, 2]. The modern versions of these methods usually employ density functional theory (DFT) computations [3–5]. These methods yield quantities that characterize the global reactivity of molecules (chemical potential, global hardness, softness, electrophilicity index, nucleophilicity index) [3–7]. For many systems, however, such information is not sufficient, since it does not describe local (atomic sites) reactivities and positional selectivities. To avoid these problems, a number of localization methods have been proposed [5, 8, 9]. Implicit in these methods are variously defined theoretical atomic charges. The accuracy of reactivity predictions in applying such procedures depends, therefore, on the particular definition of atomic charges. Computed atomic charges are frequently employed in rationalizing chemical reactivity [10–19]. A considerable advantage of these quantities is their straightforward physical interpretation. An alternative to these methods is the application of the molecular electrostatic potential (MESP) [20, 21]. MESP maps as well as minimum and maximum MESP values (V_{min}, V_{max}) have been successfully applied in quantifying chemical reactivity, especially for processes, where the electrostatic interaction between the reactants is important [22–25]. It should be underlined that MESP computations do not involve additional approximations aside from those inherent in evaluating the molecular wave function. We have proposed the electrostatic potential at nuclei (EPN, V_Y) as a local reactivity descriptor and have shown that EPN quantifies the reactivity of molecules toward hydrogen bonding as well as for a number of chemical reactions [26]. EPN was first introduced by Wilson in 1962 [27]. Politzer and Truhlar [20] defined the potential at nuclei Y by the expression:

$$V_Y \equiv V(\mathbf{R}_Y) = \sum_{A(\neq Y)} \frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_Y|} - \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_Y|} d\mathbf{r} \qquad (1)$$

In Eqn. 1, R_A and Z_A are the position vector and the charge of nucleus A. $\rho(\mathbf{r})$ is the electron density

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function. The singular term $R_A = R_Y$ is excluded. In essence, the V_Y value reflects the potential at the position of nucleus Y (R_Y), determined by the positive charges of all nuclei except nucleus Y and the entire electron density. This definition of V_Y limits the applicability of this quantity in rationalizing reactivities only to series of structurally related molecules. Providing that the structural changes in such series be at some distance to the reaction center, the shifts of V_Y follow quite well the variations in the electron density near atom Y [28].

In the present research, we focus on examining by theoretical methods a series of 37 substituted pyridines. Extensive experimental data on the proton affinities (PA) and basicities (pK_b) of these systems are available [29, 30]. Both of these properties are inherently associated with the chemical reactivity of the molecules. These data offer an excellent opportunity for testing the performance of alternative theoretical quantities in characterizing and predicting these properties.

Herein, we report results from the application of Hirshfeld [31] and NBO [32] atomic charges and of the electrostatic potential at nuclei in analyzing and predicting both experimental (basicities, pK_b, and proton affinities, PA) and theoretical (hydrogen bonding energies) quantities for a series of 37 3- and 4-monosubstituted pyridines. Popelier *et al.* [33] correlated the basicities of substituted pyridines with electron density parameters derived from the Atoms in Molecule (AIM) approach. A multiparameter analysis yielded in good correlations for 3- and 4-substituted derivatives. Hopkins *et al.* [34] have established a good correlation between experimental relative hydrogen bonding basicities and the gas-phase proton affinities for a series of nineteen 3- and 4-substituted pyridines. Blanco *et al.* [35] conducted a theoretical study (at B3LYP/6-31+G**) of the effects of monosubstitution in pyridines involving the atoms from the second and third rows in the periodic table. These authors established an excellent correlation between theoretically estimated proton affinities and MESP minimum values. Theoretical computations using semi-empirical molecular orbital computations have also been applied in examining the substituent effects on the pK_a values in nitrogen containing organic compounds including pyridines [36]. Habbibi-Yangjeh *et al.* [37] applied a combined principal component analysis-genetic algorithm-neural network approach in predicting the basicities of substituted pyridines.

COMPUTATIONAL METHODS

The geometries of reactants, complexes between substituted pyridines and HF, and H_2O, respectively, were fully optimized using the ωB97X-D hybrid functional [38], combined with correlation-consistent aug-cc-pvtz basis set [39]. The ultrafine grid was used for the numerical integrations. The interaction energies were corrected for the basis set superposition error by the Boys-Bernardi counterpoise method [40] in all the complexes. Harmonic vibrational frequency computations were evaluated to ensure that the optimized structures are true minima. All computed parameter values refer to isolated molecules and complexes in the gas phase. The computations employed the Gaussian 09 program package [41]. Cartesian coordinates and energies of all optimized structures are given in the Supplementary Material.

RESULTS AND DISCUSSION

The conducted computations include complete optimizations of isolated pyridine derivatives and their hydrogen bonded complexes with two model proton donating molecules: hydrogen fluoride and water. The employed ωB97X-D density functional has been shown to perform well for both thermochemistry and noncovalent interactions [42]. Besides, Medvedev *et al.* [43] reported recently that the inherent in these computations B97 hybrid functional [44] is among the best performing functionals in deriving the electron density distributions in molecules. As emphasized, the present research centres on examining how well charge related parameters (atomic charges, electrostatic potentials) correlate with the experimental basicities and proton affinities as well as with theoretically derived hydrogen bonding energies. Table 1 presents the results for NBO and Hirshfeld charges at the pyridine nitrogen for the series of monomeric 3- and 4-substituted derivatives. The shifts of the electrostatic potential at the nitrogen atom with respect the unsubstituted pyridine (ΔV_N) are shown in column five. Table 1 contains also the computed hydrogen bonding energies (ΔE) for the complexes with HF and H_2O and the experimental pK_b and gas-phase proton affinities. The last four rows of Table 1 contain the correlation coefficients for the relationships between the theoretical parameters (q^{NBO}, $q^{Hirshfeld}$, ΔV_N) and the considered experimental (pK_b, PA) and theoretical (ΔE) values. Figure 1 illustrates some of these relationships. As expected, the correlations between ΔV_N and the hydrogen bonding energies (ΔE) are excellent. The correlation coefficient for the complexes with hydrogen fluoride is $\boldsymbol{r} = 0.993$. Energy decomposition analysis has shown a very strong participation of the electrostatic energy term in hydrogen bonding [45].

Table 1. ωB97X-D/aug-cc-pvtz calculated values of atomic charges, experimental basicities (pK_b)[a] and proton affinities (PA)[b] of 3-, and 4-substituted pyridines, and complexation energies (ΔE=Eel+ZPC+BSSE) of hydrogen bonding complexes between the pyridines and HF (ΔE^{HF}) and H_2O (ΔE^{water})

	subs.	q_N^{NBO} [a.u.]	$q_N^{Hirshfeld}$ [a.u.]	ΔV_N[c] [volt]	pK_b	PA [kcal mol^{-1}]	ΔE^{HF} [kcal mol^{-1}]	ΔE^{water} [kcal mol^{-1}]
1	H	–0.428	–0.167	0.000	8.83	222.28	–11.30	–5.15
2	*3*-Br	–0.410	–0.156	0.396	11.15	217.50	–10.16	–4.62
3	*3*-C(CH$_3$)$_3$	–0.423	–0.169	–0.149	8.18	–	–11.82	–5.48
4	*3*-CH(CH$_3$)$_2$	–0.423	–0.169	–0.130	8.28	–	–11.74	–5.43
5	*3*-CH$_2$CH$_3$	–0.423	–0.168	–0.115	8.20	226.44	–11.69	–5.39
6	*3*-CH$_3$	–0.423	–0.168	–0.107	8.32	225.48	–11.66	–5.35
7	*3*-Cl	–0.410	–0.156	0.392	11.16	215.92	–10.16	–4.58
8	*3*-CN	–0.416	–0.153	0.748	12.55	209.61	–9.14	–4.19
9	*3*-COCH$_3$	–0.431	–0.165	0.321	10.74	218.98	–10.63	–4.97
10	*3*-CONH$_2$	–0.422	–0.159	0.244	10.67	219.48	–10.42	–4.92
11	*3*-COOCH$_3$	–0.430	–0.163	0.244	10.87	221.23	–10.72	–4.86
12	*3*-COOCH$_2$CH$_3$	–0.430	–0.164	0.211	10.65	–	–10.82	–4.95
13	*3*-COOH	–0.428	–0.162	0.347	11.93	–	–10.37	–4.71
14	*3*-F	–0.407	–0.156	0.358	11.03	215.59	–10.32	–4.66
15	*3*-NH$_2$	–0.408	–0.165	–0.141	7.97	228.11	–11.88	–5.49
16	*3*-NHCOCH$_3$	–0.408	–0.159	–0.037	9.63	–	–11.17	–5.31
17	*3*-NO$_2$	–0.415	–0.151	0.818	13.21	–	–9.05	–4.24
18	*3*-OCH$_3$	–0.408	–0.162	–0.032	9.09	225.31	–11.38	–5.20
19	*3*-OH	–0.407	–0.162	0.110	9.20	222.16	–11.17	–5.26
20	*3*-SCH$_3$	–0.412	–0.160	0.063	9.58	223.83	–10.97	–5.08
21	*4*-Br	–0.426	–0.164	0.294	10.29	219.36	–10.54	–4.73
22	*4*-C(CH$_3$)$_3$	–0.435	–0.174	–0.208	8.01	228.90	–12.00	–5.48
23	*4*-CH(CH$_3$)$_2$	–0.436	–0.174	–0.185	7.98	228.42	–11.86	–5.44
24	*4*-CH$_2$CH$_3$	–0.436	–0.174	–0.172	8.13	227.32	–11.81	–5.42
25	*4*-CH$_3$	–0.437	–0.174	–0.164	8.00	226.39	–11.77	–5.40
26	*4*-CH=CH$_2$	–0.430	–0.169	–0.047	8.38	225.65	–11.46	–5.20
27	*4*-Cl	–0.429	–0.165	0.275	10.17	218.96	–10.57	–4.76
28	*4*-CN	–0.405	–0.150	0.734	12.10	210.47	–9.44	–4.20
29	*4*-COCH$_3$	–0.410	–0.157	0.321	10.50	218.62	–10.57	–4.89
30	*4*-COOCH$_3$	–0.410	–0.157	0.270	10.74	221.47	–10.66	–4.84
31	*4*-COOCH$_2$CH$_3$	–0.411	–0.158	0.237	10.55	–	–10.69	–4.86
32	*4*-COOH	–0.407	–0.154	0.380	12.16	–	–10.35	–4.65
33	*4*-NH$_2$	–0.469	–0.192	–0.486	4.89	234.16	–12.79	–5.92
34	*4*-NO$_2$	–0.400	–0.147	0.811	12.77	208.97	–9.26	–4.10
35	*4*-OCH$_3$	–0.457	–0.184	–0.279	7.53	229.86	–12.06	–5.55
36	*4*-OCH$_2$CH$_3$	–0.458	–0.185	–0.319	7.33	–	–12.20	–5.66
37	*4*-SCH$_3$	–0.443	–0.176	–0.113	8.06	228.30	–11.58	–5.32
r with pK_b		0.681	0.906	**0.965**; y = 5.457x + 8.976				
r with PA		0.695	0.894	**0.988**; y = –19.29x + 224.5				
r with ΔE^{HF}		0.651	0.890	**0.993**; y = 2.753x – 11.34				
r with ΔE^{water}		0.633	0.874	**0.987**; y = 1.352x – 5.212				

[a] From ref. [29]. [b] From ref. [30]. [c] $\Delta V_N = V_N(Y–C_5H_4N) – V_N(C_5H_5N)$.

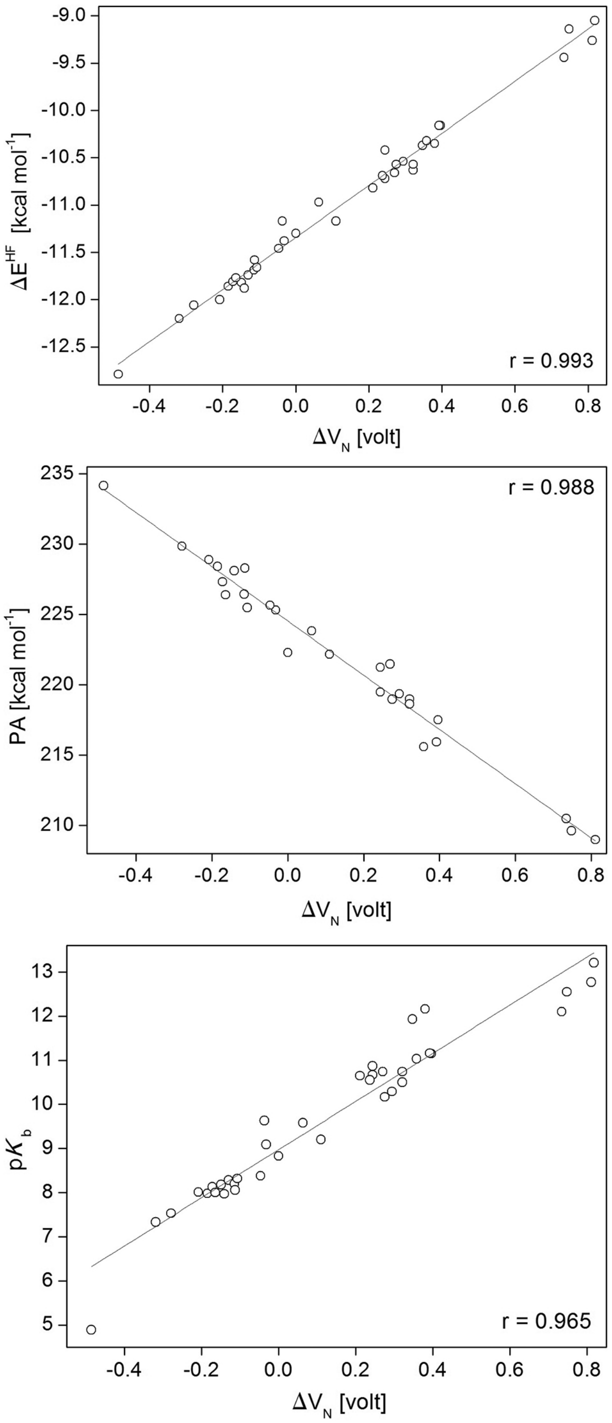

Fig. 1. Dependences between the theoretical electrostatic potential at the N atom in 3- and 4-monosubstituted pyridines and theoretically evaluated hydrogen bonding energies for complexes with HF (ΔE) as well as with the experimental basicities (pK_b) and proton affinities (PA).

An excellent correlation of ΔV_N with the experimental proton affinities for the substituted pyridine is also established (***r*** = 0.988). As expected, electrostatic effects dominate the interaction of the pyridine nitrogen lone pair with the incoming proton. The dependency between shifts of electrostatic potential with basicities (pK_b) is still satisfactory (***r*** = 0.965) though with lower correlation coefficient. The pK_b values refer to equilibrium in water solution. Thus, very high linearity with the computed for the gas-phase shifts of electrostatic potentials at the pyridine nitrogen may not be expected. Still, the found relationship for 37 substituted pyridine may be used in predicting, at least qualitatively, basicity values.

The two tested atomic charges (NBO and Hirshfeld) do not provide satisfactory correlations with the studied theoretical and experimental quantities (Table 1). Nonetheless, the Hirshfeld charges perform better than the NBO atomic charges for all studied relationships. Popelier and Green [46] have discussed that hydrogen fluoride may not be the best choice for a model proton-donating species in describing basicities of molecules. These authors quantified the basicities of a series of 41 organic bases belonging to different classes in terms of the change of the energy of the proton-donating molecule in going from monomer to complex. Employing water as a model hydrogen donor resulted in much improved correlations. In view of these results, we conducted additional computations for the series of 37 pyridine derivatives using water as a model proton-donating species. The computed hydrogen bonding energies are given in the last column of Table 1. The correlation coefficients for the relationships with q^{NBO}, $q^{Hirshfeld}$, and ΔV_N are shown in the last row of the table. For the present series of pyridine derivatives, the obtained correlations with atomic charges and ΔV_N confirm the reported results for the complexes with hydrogen fluoride.

CONCLUSIONS

The results from this research outline a simple approach in analyzing and predicting properties for series structurally related molecules using theoretical computations. The conducted investigation considered experimental proton affinities (PA), experimental basicities (pK_b), and theoretically evaluated hydrogen bonding energies (ΔE) for 37 pyridine derivatives with substituents at positions 3 and 4. ωB97X-D/aug-cc-pVTZ computations provided the theoretical NBO charges, Hirshfeld charges, and electrostatic potential at nuclei (EPN) values, all associated with the nitrogen atom in the isolated pyridines. Among the three tested theoretical parameters, the electrostatic potential at the nitrogen (V_N) provides the best predictive potential for the properties considered.

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ПРЕДСКАЗВАНЕ НА МОЛЕКУЛНИ СВОЙСТВА С ПОМОЩТА НА ТЕОРЕТИЧНИ ПАРАМЕТРИ: ЗАМЕСТЕНИ ПИРИДИНИ

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(Резюме)

Потенциалът на три алтернативни теоретични величини – NBO атомни заряди, Hirshfeld заряди и електростатични потенциали върху ядрата (EPN) – да предсказват молекулни свойства е оценен при проучване върху серия от 37 заместени пиридинови производни. Тези молекулни параметри са определени с помощта на изчисления, ползващи теорията на плътностния функционал с метода ωB97X-D/aug-cc-pVTZ. Корелации с експериментално определени константи на базичност (pK_b), както и с теоретично определени енергии на водородно свързване (за комплекси с HF и H_2O), показват, че измежду изследваните параметри, стойностите на EPN за позицията на пиридиновия азотен атом, предоставят най-добри възможности за предсказване на молекулни свойства при пиридинови производни.