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THEORETICAL STUDY OF IONIZATION POTENTIALS OF N-HETEROCYCLIC COMPOUNDS

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Abstract

The ability to predict the redox properties is an important tool for study electron transfer processes occurring in the gas-phase (atmospheric chemistry) or in the condensed phase (electrochemistry, biochemistry). MPWB1K/6-31+G(d) and MPWB1K/tzvp theoretical models were found to provide reasonable accuracy of the prediction of ionization potentials for mono- and polycyclic azacompounds. The root mean square errors of the methods are 0.19 and 0.20, respectively. While the mean absolute deviation for both methods is the same and equals to 0.15 eV. These theoretical models were applied to predict ionization potentials for compounds not evaluated experimentally. Influence of substitutes and a number of nitrogen atoms on value of ionization potential was analyzed. Methyl-, and phenyl- groups, and fused benzo cycle decrease ionization potentials of N-heterocycles. Increase of amount of nitrogen atoms in five-membered cycles leads to significant enlargement of ionization potentials.

Keywords: azacyclic compounds, DFT, ionization potential.

ТЕОРЕТИЧНЕ ДОСЛІДЖЕННЯ ПОТЕНЦІАЛІВ ІОНІЗАЦІЇ N-ГЕТЕРОЦИКЛІЧНИХ СПОЛУК

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Анотація

Доведено, що теоретичні моделі MPWB1K/6-31+G(d) і MPWB1K/tzvp забезпечують гарну точність прогнозу потенціалів іонізації для моно- і поліциклічних азасполук. Середньоквадратичне відхилення методів становить 0,19 і 0,20 відповідно, у той час як середнє абсолютне відхилення для обох методів однакове і дорівнює 0,15 еВ. Ці теоретичні моделі було застосовано для прогнозування потенціалів іонізації сполук, для яких відсутні відповідні експериментальні дані. Проаналізовано вплив замісників та кількості атомів Нітрогену на величину потенціалу іонізації. Метильна і фенільна групи, а також конденсоване бензольне ядро зменшують потенціали іонізації N-гетероциклів. Збільшення кількості атомів Нітрогену в п’ятичленних циклах обумовлює значне зростання потенціалів іонізації.

Ключові слова: азациклічні сполуки, ТФГ, потенціал іонізації.

ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ ПОТЕНЦИАЛОВ ИОНИЗАЦИИ N-ГЕТЕРОЦИКЛИЧЕСКИХ СОЕДИНЕНИЙ

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Аннотация

Доказано, что теоретические модели MPWB1K/6-31+G(d) и MPWB1K/tzvp обеспечивают хорошую точность прогноза потенциалов ионизации для моно- и полициклических азасоединений. Среднеквадратичная погрешность методов равна 0,19 и 0,20 соответственно, в то время как среднее абсолютное отклонение для обоих методов одинаково и равно 0,15 эВ. Эти теоретические модели были применены для прогнозирования потенциалов ионизации соединений, для которых отсутствуют соответствующие экспериментальные данные. Проанализировано влияние заместителей и количества атомов азота на величину потенциала ионизации. Метильная и фенильная группы, а также конденсированое бензольное ядро уменьшают потенциалы ионизации N-гетероциклов. Увеличение количества атомов азота в пятичленных циклах приводит к значительному возрастанию потенциалов ионизации.

Ключевые слова: азациклические соединения, ТФП, потенциал ионизации.

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Introduction

Redox reactions are widely spread in nature and used in industry. Knowledge of electrochemical properties of compounds is highly desirable to understand the nature of electron-transfer reactions and the determination of molecular characteristics. Sometimes, not only the magnitude but even the sign of redox characteristics are difficult to experimental measure. In those cases, the theoretical prediction of such properties as ionization potential, electron affinity, reduction and oxidation potentials is used. In this context the search of methods to accurately predict redox properties has a great interest of chemical community. Different approaches were examined for some classes of organic compounds [1-10]. Some of the predictions are quite accurate (errors are in a range of 0.1-0.2 eV) and cover a wide range of classes of organic molecules. The present study continues our work in prediction of one electron oxidation properties for nitrogen-containing heterocyclic compounds [8; 9]. Earlier we obtained a good accuracy in prediction of electron attachment energy for azacyclic compounds, quinones and nitrocompounds at the MPWB1K/tzvp level of theory [8]. The aim of this study is to establish a computational protocol that accurately calculates ionization potentials (IPs) for N-heterocyclic compounds and is able to predict redox properties for compounds where experimentally measured potentials are unavailable. For the present study 29 mono- and polycyclic azacompounds containing five, and six-membered rings with available experimental IPs were chosen (see Fig. 1). These compounds contain varying numbers of nitrogen atoms in a heterocycle.

Computational Details

All of the calculations were performed using the Gaussian 09 program package [11]. The geometry of neutral, and radical species were optimized at MPWB1K/6-31+G(d) and MPWB1K/tzvp levels of theory [12].Harmonic vibrations were calculated for all structures obtained to establish that a minimum was observed. IPs were calculated as the electronic energy difference between cation-radical oxidized and neutral reduced forms corrected by zero-point energy.

Results and Discussion

Calculated IPs of azacompounds were compared with experimental data. Table 1 summarizes the calculated and available experimental values of IPs, the Root Mean Square Error (RMSE), and Mean Absolute Deviation (MAD). Calculated IPs are in a good agreement with experimental data: MAD is 0.15 eV, correlation coefficient is 0.96 (Fig. 2). MPWB1K functional gave slightly better results with the 6-31+G(d) basis set as compared to the tzvp basis. The RMSE was found to be 0.19 and 0.20, respectively. Since the present functional and basis sets are able to provide the accuracy closed to experimental measurements they were used to predict IPs for azacyclic compounds (30-44) with unmeasured ionization energy to the best of our knowledge (Table 1).

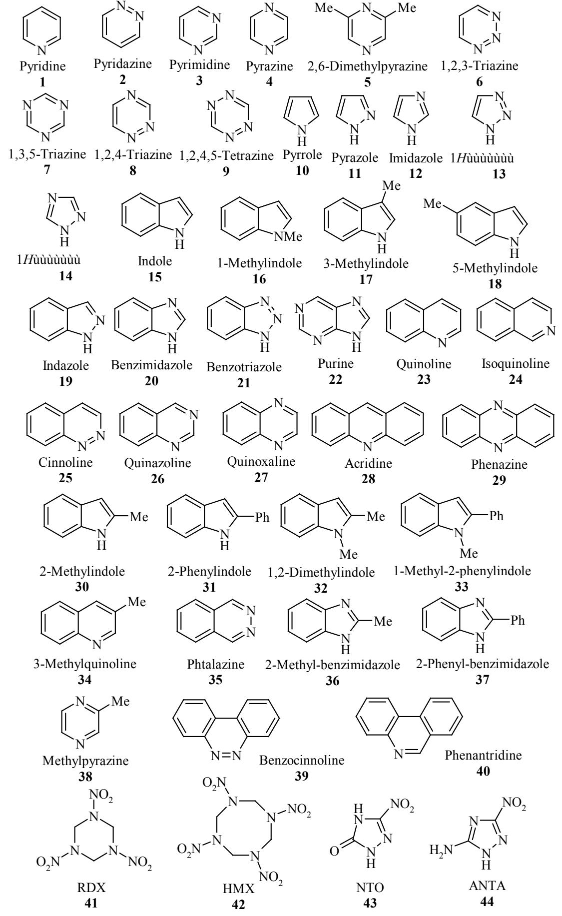


Fig. 1. Numbering of considered compounds

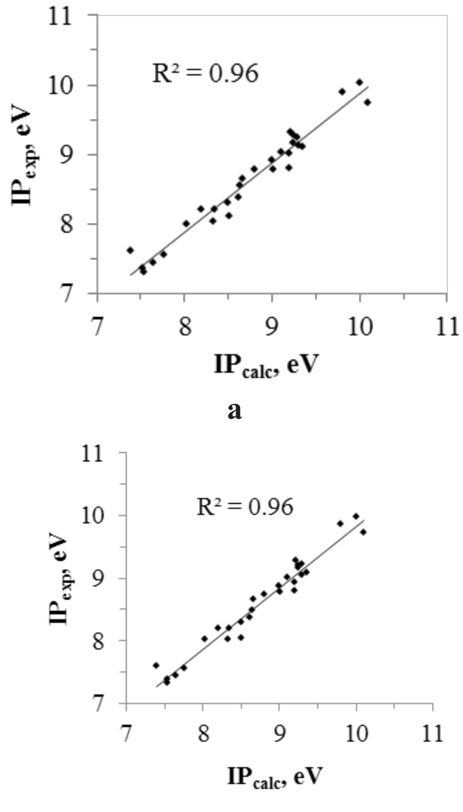
Table 1

Calculated and available experimental ionization potentials E^0_{red} (eV) of azacyclic compounds (1-44), RMSE and MAD of calculated values *vs.* experimental data

Compound number	Calc.		Exp.[13]
	MPWB1K/6-31+G(d)	MPWB1K/tzvp	
1	9.03	9.00	9.10
2	8.54	8.48	8.64
3	9.32	9.28	9.21
4	9.25	9.22	9.29
5	8.78	8.74	8.80
6	9.14	9.06	9.30
7	10.03	9.99	10.01
8	9.00	8.94	9.20
9	9.28	9.21	9.24
10	8.00	8.02	8.02
11	9.16	9.16	9.25
12	8.65	8.66	8.81
13	9.74	9.73	10.10

Table 1 (continued)

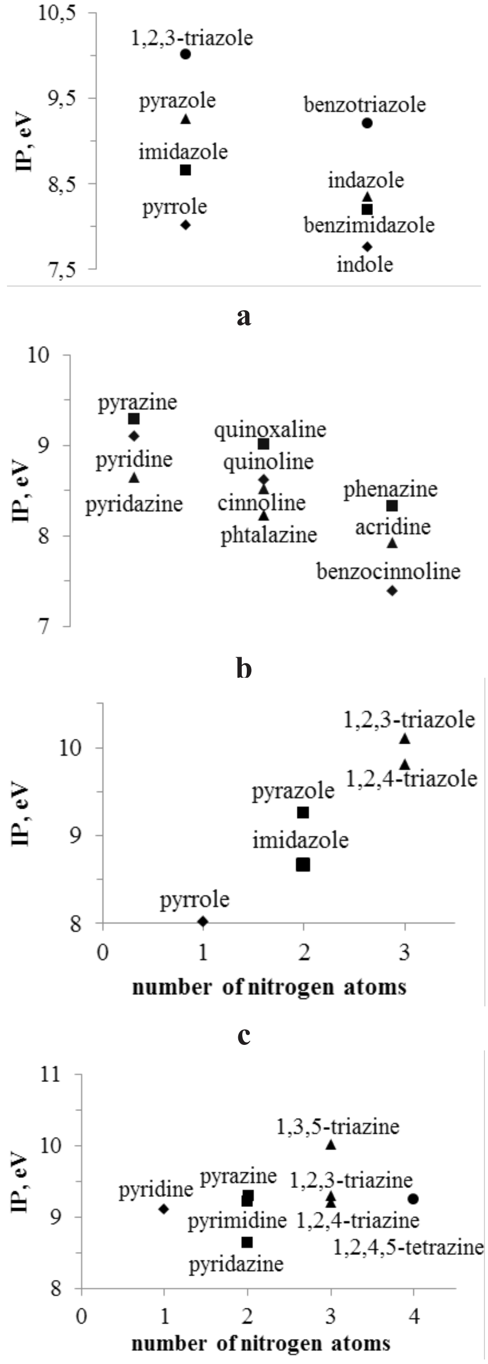
Compound number	Calc.		Exp.[13]
	MPWB1K/6-31+G(d)	MPWB1K/tzvp	
14	9.89	9.87	9.80
15	7.56	7.57	7.76
16	7.37	7.38	7.40
17	7.31	7.32	7.51
18	7.43	7.44	7.38
19	8.20	8.21	8.35
20	8.20	8.20	8.20
21	8.80	8.79	9.20
22	9.10	9.10	9.35
23	8.38	8.38	8.62
24	8.29	8.29	8.50
25	8.11	8.04	8.51
26	8.91	8.88	9.00
27	8.79	8.77	9.01
28	7.60	7.60	7.39
29	8.04	8.03	8.33
30	7.28	7.28	–
31	7.06	7.06	–
32	7.12	7.12	–
33	6.99	7.00	–
34	8.20	8.19	–
35	8.18	8.10	–
36	7.89	7.88	–
37	7.51	7.51	–
38	9.00	8.96	–
39	7.88	7.79	–
40	8.07	8.06	–
41	10.61	10.55	–
42	10.32	10.22	–
43	9.77	9.75	–
44	9.24	9.21	–
RMSE	0.19	0.20	
MAD	0.15	0.15	



a

b

Fig. 2. Plots of experimental ionization potentials E^0_{red} (eV) of azacyclic compounds vs. calculated data: a - MPWB1K/6-31+G(d); b - MPWB1K/tzvp



a

b

c

d

Fig. 3. MPWB1K/6-31+G(d) calculated ionization potentials E^0_{red} (eV) of azacyclic compounds

As can be seen from the Table 1 and Fig. 3 substitutes affect on the value of IP of heterocycles. Methyl- and phenyl- groups decrease IP by 0.1-0.4 eV and 0.5-0.6 eV, respectively. Fused phenyl cycle reduces IP by 0.5-0.9 eV and 0.1-0.5 eV in five- and six-membered heterocycles, respectively (Fig. 3a,b). Increase of number of nitrogen atoms in five-membered cycles leads to a significant enlargement of IP about 0.6-1.2 eV (Fig. 3c). While in case of six-membered heterocycles the correlation between IP and the number of nitrogen atoms in cycle is not observed (Fig. 3d).

Conclusions

MPWB1K/6-31+G(d) and MPWB1K/tzvp methods have been found to provide a good agreement with experiment, and may be used for realistic calculations of IP of azacyclic compounds. Alkyl and phenyl substitutes decrease the value of IP. While the increase of nitrogen atoms in a five-membered cycle enlarges IP.

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