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АНАЛИЗ РАЗЛИЧНЫХ БАЗ ДАННЫХ ДЛЯ ПОТЕНЦИАЛОВ ИОНИЗАЦИИ И СРОДСТВА К ЭЛЕКТРОНУ ХИНОНОВ НА ОСНОВЕ ВЫЧИСЛЕНИЙ С ИСПОЛЬЗОВАНИЕМ ТЕОРИИ ФУНКЦИОНАЛА ПЛОТНОСТИ

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Исследование имеет отношение к решению теоретической проблемы изучения хинонов как представителей природных и синтетических соединений с большим разнообразием применений в химическом катализе, биохимических и технических областях науки. Для этого выбран метод компьютерной химии в качестве развитого инструмента для оценки электронных энергий простых хининов, нафтохинонов и антрахинонов, являющихся родоначальниками более сложных соединений. Проведены вычисления потенциалов ионизации и сродства к электрону 88 простых хинонов на основе использования метода B3LYP теории функционала плотности с различными базисными функциями, и на этой основе проведена оценка различных баз данных для энергий электронов. База данных для сродства к электрону включает опубликованные результаты измерений абсолютных значений сродства к электрону π-комплексов переноса заряда и данные, основанные на измерении относительных величин при изучении равновесия этого процесса. Найдена нелинейная квадратичная корреляция между вычисленными и экспериментальными значениями. Анализ относительных отклонений расчетных значений от экспериментальных данных указывает на высокое качество базы данных, представаленой в исследовании Хилала с сотр., основанной на измерении относительных равновесных величин переноса электронов. Результаты, найденные в исследовании, применимы для оценки корректности расчетных методов и экспериментальных для энергий электронов в ряду хинонов.

Ключевые слова: ДФТ, потенциал ионизации, сродство к электрону, хиноны

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ANALYSIS OF DIFFERENT DATASETS FOR IONIZATION POTENTIAL AND ELECTRON AFFINITY OF QUINONES ON THE BASIS OF DFT CALCULATIONS

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The idea of this research deals with theoretical problems of studying quinones as representatives of natural and synthetic compounds with a huge variety of applications in chemical catalysis, biomedical and technical sciences. For this purpose computational chemistry is chosen as an advanced tool for evaluating electronic energies in gase phase for a series of simple quinones, naphthoquinones and anthraquinones as parent compounds for more complicated ones.

Ionization potentials and electron affinities (IPs and EAs) of 88 quinones are calculated by the use of B3LYP level of density functional theory (DFT) with different basis sets, and on this base the validation of several databases for electronic energies of quinones is done. The databases for EAs include published results of measurements of absolute electron affinities of pi charge transfer complex acceptors and those determined as relative values from electron transfer equilibrium studies. Non-linear quadratic correlation was found for relationship between calculated and experiment values of electron affinities. Analysis of the relative deviation between obtained calculated results and the three experimental databases indicated the high quality of the database proposed by Hilal et al. based on electron transfer equilibrium studies. The results found in the research are applicable for validation of computational methods and experimental data for electronic energies of quinones.

Key words: DFT, ionization potential, electron affinity, quinones

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INTRODUCTION

Quinones and their derivatives receive much attention as a big group of natural and synthetic compounds of wide applications due to very pronounced redox effects in chemical reactions. Numerous quantum chemical computational research is being done recently for quinones, such as [1-10], for deeper understanding the mechanisms of different processes. Recent research in computational quantum chemistry [1-13] has reached the level of predicting of hydration (solvation) energy and redox potentials of organic compounds in solution as well as their spectral properties in different solvents.

Development of the methods of computational analysis increases interest to experimental data collected in different previous research. Usually applied research goes ahead of fundamental studies and very often there is a lack of experimental data, which could form a basis for future analysis. The amount of chemical databases already reached saturation or even decreased in their development [14]. Therefore virtual screening is being developed for the needs of modern applied research based on above mentioned quantum chemical calculations or QSPR studies [14-21].

One of the good examples of virtual screening of about 1500 thiophenquinone derivatives with prior calculation of redox and solvation properties is proposed in the research of lithium redox flow batteries [22, 23]. Similar approach for less amount of anthraquinone derivatives was proposed in the research [23, 24]. Other fields of application of quinones, such as medicine and drugs, ecological problems, photovoltaic techniques, etc. also need an advanced prognosis of physico-chemical and technical properties as well as biological activity of quinoid compounds by the use of virtual screening.

One of the most important fundamental properties of atoms and molecules are ionization potentials (IPs) and electron affinities (EAs) characterizing their electron donating and accepting ability. Some theoretical and experimental studies [25-31] have been carried out to study the IP and EA of different compounds including simple quinone and anthroquinone derivatives. The calculated IPs and EAs of quinones are both important for development of theory, methods of computations and experimental evaluation. For example, ionization energy of different compounds including quinones in gase phase is used for predicting their redox potential in solution on the basis of well-defined correlations of those two quantities [4, 7, 25, 32, 33]. From another side, this close relationship is used for calculation electron affinity by polarographic technique, as it was analysed in [25]. In general, this kind of correlation is an important part of development of solvation theory [34-36] and analysis of different compounds, like aliphatic hydrocarbons [37], aromatic hydrocarbons [38], benzyl and biphenyl derivatives [32,39], substituted anilines [40], hetaryls [41], azoalkanes [42], polycyclic aromatic hydrocarbons [43], pentacenes [44], benzothiophene [45], ferrocene derivatives [46], etc.

The above analysis shows that very few systematic experimental results are published for IPs and EAs of quinone derivatives, while theoretical calculations cover limited amount of compounds [25-30] or only theoretical results are reported without comparison with experiment [4, 31].

This research is aiming to calculate IPs and EAs of 88 quinones by the use of density functional theory (DFT) B3LYP method with different basis functions and on this ground to make a validation of several databases for electronic energies of quinones. Further research will be focused on computational evaluation of redox potentials of those compounds in solution by the use of recently developed methods mentioned above.

Different basis sets are used for DFT B3LYP level of theory, such as 6-311+G(d) and 6-311G(d). The experimental values of ionization energies, IP and EA, reported by Gurvich [28], Chen [25], Hilal [26] and Fukuda [27] were used to study the correlations with calculated ones. The EAs calculated in Frontana's [29] and Zhu's [30] research were used for comparison of those calculated in our study. Based on the correlation coefficient of calculated and experiment EA and IP values, IP and EA values of other more complicated quinones were theoretically proposed. Finally, the quality of experimental data from collected datasets were evaluated, that offers important reference for researchers in this filed.

EXPERIMENTAL DATABASE AND COMPUTATIONAL METHODS

Several databases for IPs and EAs of quinone derivatives were selected for evaluation their quality [25-28]. According to the above references results for EAs by Chen et al [25] are based on measurements of absolute electron affinities of pi charge transfer complex acceptors by magnetron method. In other research [26, 27] EAs were determined with electron transfer equilibrium techniques. Gase phase ion-molecular equilibrium measurements were performed with ion cyclotron resonance (ICR) spectrometer in method of Fukuda et al [27], and pulsed electron high ion source pressure mass spectrometer (PHPMS) in method of Hilal et al. [26]. The last two methods give relative values of EAs with reference to any compound with known value of electron affinity. IP values were obtained with polarographic method using half-wave reduction potentials in dimethylformamide and evaluated solvation energy of compounds [28]. The total database is arranged by the use of JChem for Excel provided by Chemaxon [47] and presented in the Tables 1-4 below.

Geometries of the molecules considered in this study were fully optimized by using gradient corrected DFT with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) [48] with the 6-31G(d) basis set [49]. Frequency calculations are performed at the same level of theory to ensure that the optimized geometries are minimal on the hypersurface of potential energy (all real frequencies) and to provide corrections for the zero-point vibrational energy (ZPVE) effects. The single point energy calculations were performed based on the optimized geometries at ground state.

IPs and EAs are obtained as the total energy differences between the neutral and the corresponding ionic systems, expressed as follows: $IP = E(+)–E(0)$, $EA = E(0)–E(-)$, where 0, + and – denotes respectively neutral molecule, cation and anion.

All of the calculations were performed with the Gaussian 09 software package [50] on a 18-processor Lenovo I2000 computer.

RESULTS AND DISCUSSION

B3LYP functional used in this study has high efficiency in calculating the electronic properties of studied organic molecules, such as ionization potentials (IP) and electron affinities (EA). The calculated results are presented below together with available experimental data [25-28].

Ionization Potential

In total, 14 representatives of quinones with available experiment IP values have been collected [28], they include simple benzoquinone, anthraquinone and naphthoquinone derivatives. The experimental values of IP are compiled in Table 1. A survey of calculated vertical IPs reveals that, in general, they are in good agreement with the corresponding experimental IPs. By performing a least square fit for all of the 14 systems, we obtain an excellent linear correlation between the experimental and calculated values shown in Fig. 1.

Table 1

Ionization potential of quinones calculated using the 6-311+G(d) basis set and experimental values provided by Gurvich (AQ=anthraquinone, BQ=Benzoquinone, NQ=Naphthaquinone)

***Таблица 1.* Потенциалы ионизации хинонов, рассчитанные с использованием 6-311+G(d) базиса, и экспериментальные значения по Гурвичу (AQ-антрахинон, BQ- бензохинон, NQ-нафтахинон)**

No.	Name	IPcalcd (eV)	IPexpt (eV) (Gurvich)
1	1-Hydroxy-9,10-AQ	8.4665	8.43
2	2-Hydroxy-9,10-AQ	8.5266	8.70
3	1,4-Dihydroxy-9,10-AQ	7.8920	7.94
4	1,5-Dihydroxy-9,10-AQ	8.2288	8.53
5	2,6-Dihydroxy-9,10-AQ	8.2671	8.63
6	1,4,5,8-Tetrahydroxy-9,10-AQ	7.4458	7.83
7	6,13-Pentacenequinone	7.7949	8.07
8	5,14,7,12-Pentacenediquinone	8.9289	9.22
9	2-Methyl-1,4-BQ	9.6695	9.78
10	1,4-NQ	9.4045	9.56
11	5-Hydroxy-1,4-NQ	8.6992	8.70
12	5,8-Dihydroxy-1,4-NQ	8.2049	8.20
13	Tetramethyl-p-BQ	8.7910	9.16
14	1,4-AQ	8.2747	8.45

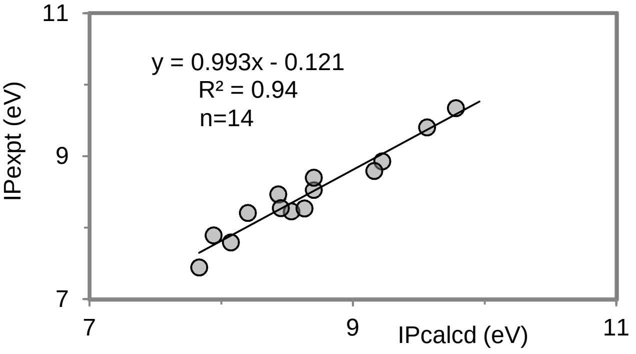
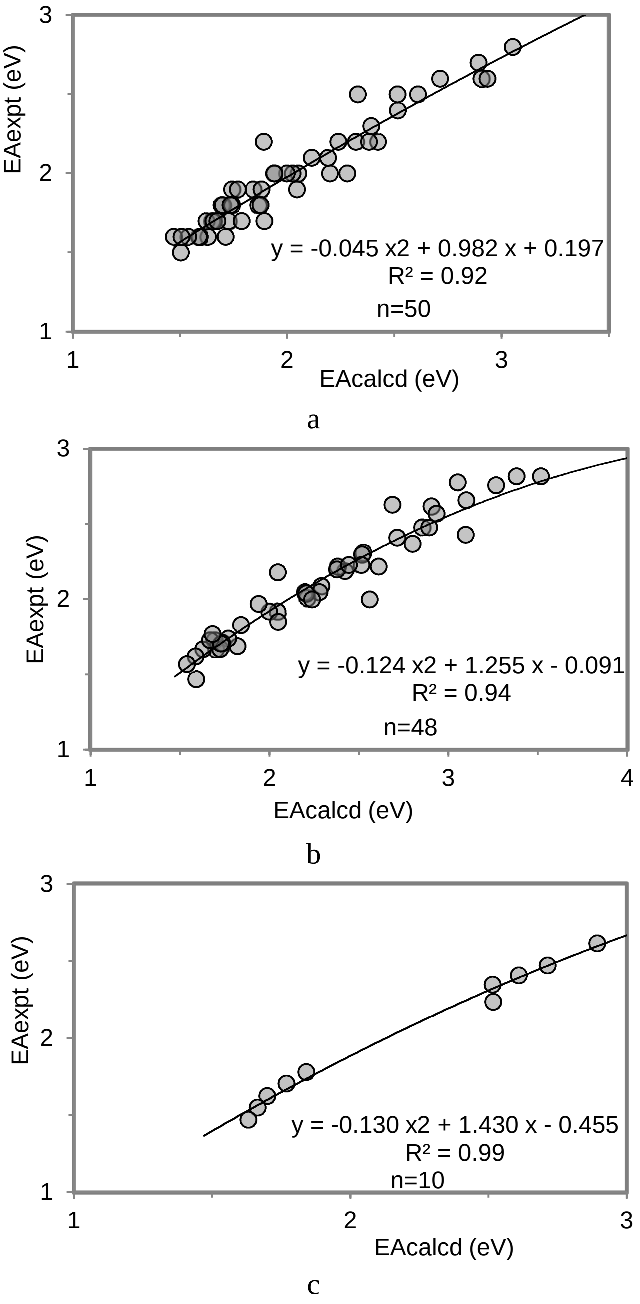


Fig. 1. Plot of calculated ionization potential IP_{calcd} (y) using 6-311+G(d) basis set versus experimental values of IP_{expt} (x) [28] (Table 1)

Рис. 1. Рассчитанные потенциалы ионизации IP_{calcd} (y) на основе 6-311+G(d) базиса как функции экспериментальных значений IP_{expt} (x) [28] (табл. 1)

Electron Affinity

A total number of 74 molecules of quinones are collected for which the experimental EAs [25-27] are available, including derivatives of benzoquinone, anthraquinone, phenanthraquinone and naphthoquinone. The experimental values of EA are compiled in Table 2. By performing a quadratic polynomial regression fit for all of the 74 systems, we found three satisfactory correlations between the available experimental data from three databases and each set of the calculated EA values. These quadratic correlations are shown in Fig. 2.



a

b

c

Fig. 2. Plot of the calculated electron affinities EA_{calcd} (y) using the 6-311G(d) basis set versus experimental values of EA_{expt} (x): a) Hilal [26], b) Chen [25], c) Fukuda [27] (see Table 2)

Рис. 2. Рассчитанные сродство к электрону EA_{calcd} (y) на основе 6-311G(d) базиса как функции экспериментальных значений of EA_{expt} (x): a) Хилал [26], b) Чен [25], Фукуда [27] (см. табл. 2)

Comparison of different databases used for calculation of electronic affinity shows, that linear term of approximating equation for correlation between calculated and experimental values varies from 0.98 to 1.43 (Fig. 2-a, b, c). So, in spite of good correlation coefficient for each database, calculated regression coefficient is most close to the experimental data provided by Hilal [26].

Table 2

Electron affinities of quinones calculated using the 6-311G(d) basis set and experimental data provided by Chen, Fukuda, Hilal

***Таблица 2.* Сродство к электрону хинонов, рассчитанное с использованием 6-311G(d) базиса и экспериментальные значения по Чену, Фукуде и Хилалу**

No	Name	EA (eV)			
		Calcd.	Expt. (Chen)	Expt. (Fukuda)	Expt. (Hilal)
1	p-BQ	1.8407	1.83	1.78	1.9
2	Acetyl-p-BQ	2.0523	2.09		2.0
3	Bromo-p-BQ	2.2115	2.01		
4	2,6-Dibromo-p-BQ	2.5253	2.31		
5	Dibromo-dimethyl-p-BQ	2.2800	2.05		2.0
6	Tetrabromo-o-BQ	2.9062	2.62		2.6
7	Tetrabromo-p-BQ	2.8533	2.48		
8	Chloro-p-BQ	2.1991	2.05		2.0
9	2-methyl-5-chloro-p-BQ	2.1152			2.1
10	2,3-Dichloro-p-BQ	2.4230	2.19		2.2
11	2,5-Dichloro-p-BQ	2.5170	2.30	2.23	2.4
12	2,6-Dichloro-p-BQ	2.5148	2.23	2.35	2.5
13	Trichloro-p-BQ	2.7137	2.41	2.47	2.6
14	Methyltrichloro-p-BQ	2.6099	2.22	2.41	2.5
15	2,5-Dimethyl-3,6-dichloro-p-BQ	2.3207			2.2
16	2,5-Dimethyl-3-chloro-p-BQ	2.0247			2.0
17	2-t-Butyl-5,6-Dichloro-p-BQ	2.3919			2.3
18	Tetrachloro-p-BQ	2.8932	2.48	2.62	2.7
19	2-t-Butyl-5-chloro-p-BQ	2.1904			2.1
20	Cyano-p-BQ	2.3813	2.22		2.2
21	2,3 Dicyano-p-BQ	3.0526	2.78		2.8
22	Tetrachloro-o-BQ	2.9344	2.57		2.6
23	Tetracyano-p-BQ	4.1521	2.87		
24	Fluoro-p-BQ	2.0461	1.92		1.9
25	Trifluoromethyl-p-BQ	2.0469	2.18		
26	Tetrafluoro-p-BQ	2.3303			2.5
27	Iodo-p-BQ	2.5606	2.00		
28	Tetraiodo-p-BQ	3.0978	2.43		
29	Methoxy-p-BQ	1.8211	1.69		
30	3,5-Dimethoxy-p-BQ	1.6488			1.7
31	2-Methyl-5,6-Dimethoxy-p-BQ	1.7421			1.9
32	Methoxycarbonyl-p-BQ	2.2068	2.04		
33	Methyl-p-BQ	1.7693	1.74	1.71	1.9
34	2,5-Dimethyl-p-BQ	1.6933	1.73		1.8
35	2,6-Dimethyl-p-BQ	1.6994	1.67	1.62	1.8
36	2-Methyl-5-isopropyl-p-BQ	1.7428			1.8
37	3-t-Butyl-p-BQ	1.8647			1.8
38	Trimethyl-p-BQ	1.6645		1.55	
39	Tetramethyl-p-BQ	1.6309	1.67	1.47	1.6
40	Dimethylamino-p-BQ	1.5917	1.47		1.6
41	3,5-Di-t-butyl-p-BQ	1.8801			1.9
42	Phenyl-p-BQ	1.9984	1.92		2.0
43	2,5-Di-t-butyl-p-BQ	1.8762			1.8
44	2,6 Dinitro-p-BQ	3.3826	2.82		
45	Nitro-p-BQ	2.6882	2.63		
46	1,2-NQ	1.7256	1.67		1.7
47	1,4-NQ	1.7355	1.71		1.8
48	2-Amino-1,4-NQ	1.6233			1.7
49	2,3-Dicyano-1,4-NQ	3.1007	2.66		
50	2,3-Dicyano-5-nitro-1,4-NQ	3.2682	2.76		
51	2,3-Dichloro-1,4-NQ	2.2389	2.00		2.2
52	2,3-Dichloro-5-nitro-1,4-NQ	2.4445	2.23		
53	2,3,5, 6-Tetrachloro-7 nitro-1,4-NQ	2.8005	2.37		
54	2,3-Dicyano-5,6-dichloro-7-nitro-1,4-NQ	3.5186	2.82		
55	5-Hydroxy-1,4-NQ	1.9399	1.97		2.0
56	2-Chloro-1,4-NQ	2.0485	1.85		
57	5-Hydroxy-1,4-NQ	1.9399	1.97		2.0
58	2-Hydroxy-1,4-NQ	1.5880	1.62		1.6
59	2-Methyl-1,4-NQ	1.6554			1.7
60	9,10-AQ	1.5384	1.57		1.6
61	1-Methyl-9,10-AQ	1.5034			1.5
62	2-Chloro-9,10-AQ	1.7881			1.7
63	2-Ethyl-9,10-AQ	1.4705			1.6
64	1,2-Dichloro-9,10-AQ	1.8902			2.2
65	2-t-Butyl-9,10-AQ	1.5069			1.6
66	1-Hydroxy-9,10-AQ	1.6680	1.73		
67	1,8-Dihydroxy-9,10-AQ	1.6742			1.7
68	1,4-AQ	1.7292	1.71		
69	9,10-Phenanthraquinone	1.6826	1.77		
70	Diphenoquinone	2.5977			

It is clear from Fig. 2 that there is a strong correlation between EAexpt and EAcalcd. Interesting, such a relationship was also observed in other research [29, 30]. However more detailed analysis in a form of relative deviation of calculated values from experimental ones shown in Fig. 3 demonstrates rather big deviations exceeding ±0.1, i.e. ±10%. Thus, Fig. 3-a, representing Hilal's data [26] have 6 molecules not in the range; Fig. 3-b, Chen's data [25], have 18 molecules not in the range and all are above 0.1; and Fig. 3-c, Fukuda's data [27], have 3 molecules not in the range and also all are above 0.1. It is evident that the minimum deviations are obtained for the good quality of Hilal's electron affinities experimental database. The minimum deviation of Hilal's database justifies the strong relationship between found calculated electron affinities and experiment electron affinities. This fact supports the validity of the use of DFT calculations for predicting electron affinities of quinones.

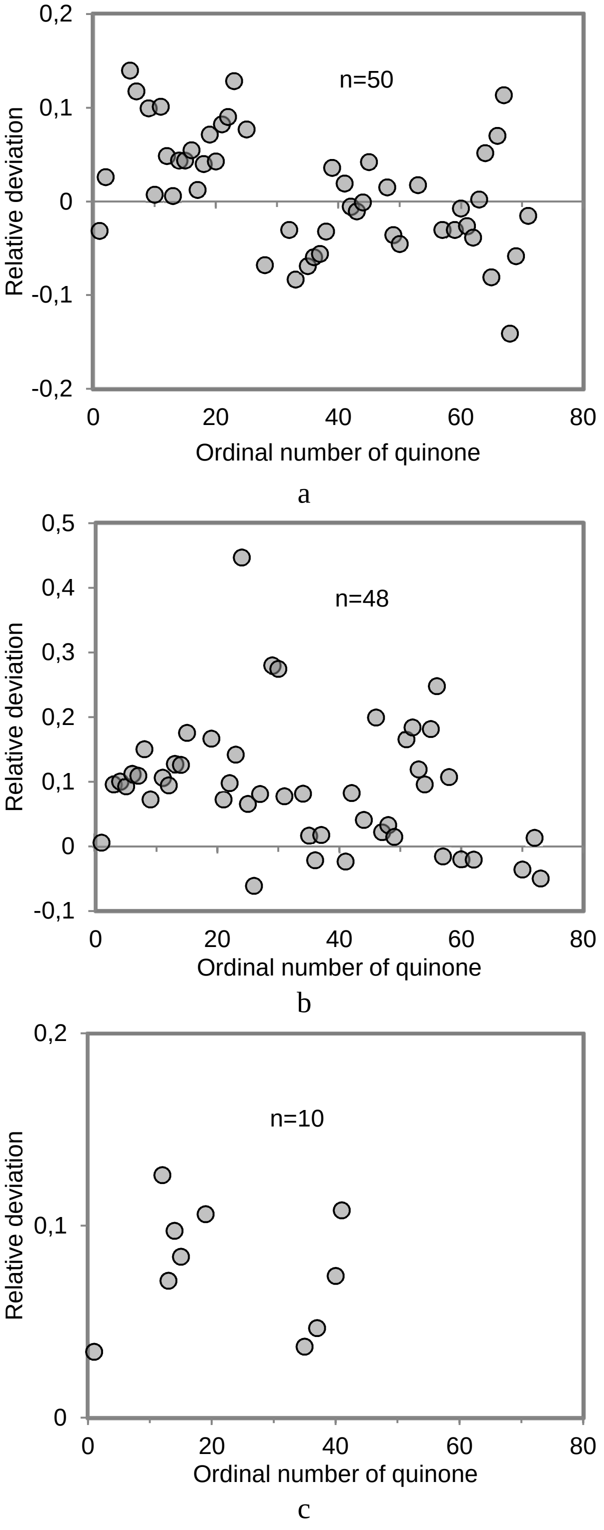


Fig. 3. Plot of relative deviation (y) of calculated electron affinities from experimental data versus ordinal number of quinone compound (x): Relative deviation = (EA_{calcd} - EA_{expt})/EA_{expt}, a) Hilal [26], b) Chen [25], c) Fukuda [27] (for number of quinone see Table 2)

Рис. 3. Относительное отклонение (y) рассчитанного электронного сродства от экспериментальных значений как функция порядкового номера хинонового соединения (x): относительное отклонение = (EA_{calcd} - EA_{expt})/EA_{expt}, а) Хилал [26], b) Чен [25], c) Фукуда [27] (нумерация хинона см. табл. 2)

It is worth of noting that EAs were obtained by Frontana [29] for 16 derivatives of quinones with the use of basis set B3LYP/6-31++G**. The calculated EA values and quinones' chemical structures are compiled in Table 3. As it is shown in Fig. 4, there is a linear correlation between those results [29] and our research with regression coefficient $R^2 = 0.90$, however, if one fluorine derivative is excluded, i.e. tetrafluorine benzoquinone, then R^2 increases up to 0.98. In general, calculated values of EA in our research are about 6% higher than Frontana's results.

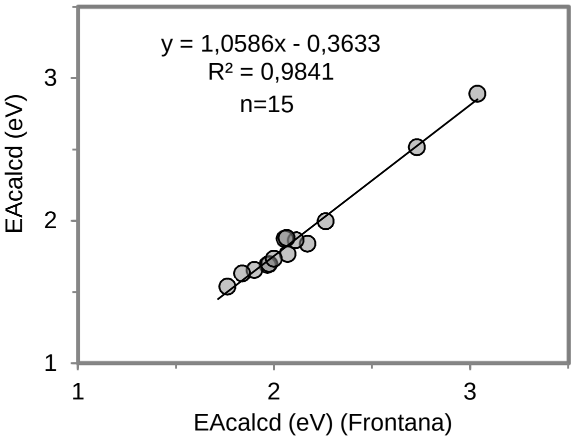


Fig. 4. Plot of EA_{calcd} (Frontana) [29] using the 6-31++G** basis set versus found EA_{calcd} values calculated using the 6-311G(d) basis set (see Table 3)

Рис. 4. Зависимость EA_{calcd} (Фронтана) [29], рассчитанная на основе 6-31++G** базиса от рассчитанных величин EA_{calcd} на основе 6-311G(d) базиса (см. табл. 3)

Table 3

Electron affinities calculated by Frontana using the 6-31++G basis set and those calculated in this research using the 6-311G(d) basis set**

Таблица 3. **Сродство к электрону, рссчитанное Фронтаной с применением 6-31++G** базиса, и рассчитанные в данной работе, и пользуя 6-311G(d) базис**

No.	Name	EA_{calcd} (eV)	EA_{calcd} (eV) (Frontana)
1	Tetrachloro-p-BQ	2.8932	3.0369
2	2,5-Dichloro-p-BQ	2.5170	2.7273
3	Phenyl-p-BQ	1.9984	2.2627
4	p-BQ	1.8407	2.1690
5	1-Methyl-p-BQ	1.7693	2.0685
6	2-t-Butyl-p-BQ	1.8647	2.1099
7	2,5-Dimethyl-p-BQ	1.6933	1.9660
8	2,6-Dimethyl-p-BQ	1.6994	1.9741
9	1,4-NQ	1.7355	1.9978
10	2,5-Di-t-butyl-p-BQ	1.8762	2.0532
11	2,6-Di-t-butyl-p-BQ	1.8801	2.0639
12	2-Methyl-1,4-NQ	1.6554	1.8991
13	Tetramethyl-p-BQ	1.6309	1.8359
14	9,10-AQ	1.5384	1.7610
15	2-Methyl-9,10-AQ		1.7135
16	Tetrafluoro-p-BQ	2.3303	3.0344

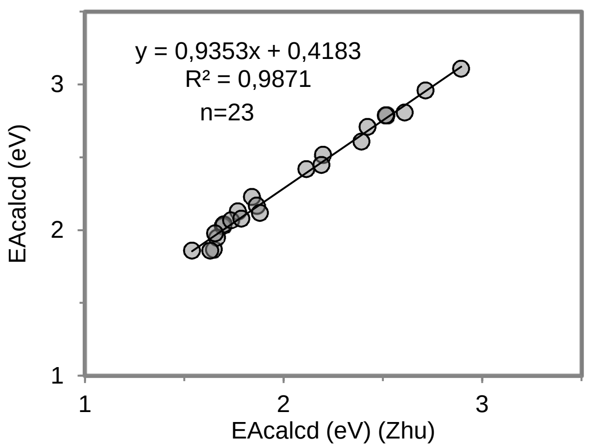


Fig. 5. Plot of EA_{calcd} (Zhu) [30] calculated using the DZP++ basis set versus found EA_{calcd} using the 6-311G(d) basis set (see Table 4)
Рис. 5. Зависимость EA_{calcd} (Джу) [30], рассчитанная на основе DZP++ базиса от рассчитанных величин EA_{calcd} на основе 6-311G(d) базиса (см. табл. 4)

Table 4

Electron affinities calculated by Zhu using the DZP++ basis set and those calculated in this research using the 6-311G(d) basis set

Таблица 4. **Сродство к электрону, рссчитанное Джу с применением DZP++ базиса, и рассчитанные в данной работе, используя 6-311G(d) базис**

No.	Name	EA_{calcd} (eV)	EA_{calcd} (eV) (Zhu)
1	p-BQ	1.8407	1.95
2	2-Methyl-p-BQ	1.7693	2.13
3	2-Chloro-p-BQ	2.1991	2.52
4	2,3-Dichloro-p-BQ	2.4230	2.71
5	2,5-Dimethyl-p-BQ	1.6933	2.03
6	2,5-Dichloro-p-BQ	2.5170	2.79
7	2,6-Dimethoxy-p-BQ	1.6488	1.87
8	2,6-Dimethyl-p-BQ	1.6994	2.04
9	2,6-Dichloro-p-BQ	2.5148	2.79
10	2,3,5-Trimethyl-p-BQ	1.6645	1.95
11	2,3,5-Trichloro-p-BQ	2.7137	2.96
12	2,3,5,6-Tetramethyl-p-BQ	1.6309	1.86
13	2,3,5,6-Tetrachloro-p-BQ	2.8932	3.11
14	1,4-NQ	1.7355	2.07
15	2-Methyl-1,4-NQ	1.6554	1.98
16	9,10-AQ	1.5384	1.86
17	2-Chloro-9,10-AQ	1.7881	2.08
18	2-t-Butyl-p-BQ	1.8647	2.17
19	2-Methyl-5-chloro-p-BQ	2.1152	2.42
20	2-t-Butyl-5,6-dichloro-p-BQ	2.3919	2.61
21	2,6-Di-t-butyl-p-BQ	1.8801	2.12
22	2-t-Butyl-5-chloro-p-BQ	2.1904	2.45
23	2-Methyl-3,5,6-trichloro-p-BQ	2.6099	2.81
24	Tetrafluoro-p-BQ	2.3303	3.08

Some other research by Zhu [30] also apply DFT calculations of EAs for 24 quinones with the use of basis set B3LYP/DZP++. The calculated EA values and quinones' chemical structures were compiled in Table 4. By comparison with the experimen-tal results [29] they found that the B3LYP/DZP++ method systematically overestimates the EAs. Similar overestimation behaviors were also found by Schaefer and co-workers [51]. In spite of the overestimation problem, it is found that the EA(B3LYP) correlate well with the experimental results, that is: EA_{expt} = 0.912EA(B3LYP) – 0.080. As it is shown in Fig. 5, there is a linear correlation between those results [30] and our research with regression coefficient $R^2 = 0.93$, however, if one fluorine derivative is excluded, i.e. tetrafluorine benzoquinone, then R^2 increases up to 0.99. As a result, calculated values of EA in our research are about 7% lower than Zhu's results.

CONCLUSION

Series of DFT calculations are performed by using a commonly used exchange-correlation functional, B3LYP, for a variety of representatives of quinones, including various derivatives of benzoquinone, anthraquinone, phenanthraquinone and naphthoquinone. It is shown that good, generally applicable quadratic correlation relationship exists between the calculated and experimental IPs. Satisfactory quadratic correlation relationships also exist between the calculated and experimental EAs. On the basis of analysis of the relative deviation between found calculated results and three experimental databases a conclusion is drawn that Hilal's database including equilibrium electron transfer energies has a minimum deviation and good quality of experimental EAs.

Comparison of different EA calculation methods shows that using the 6-311G(d) basis set correlate with 6-31++G** and DZP++ basis sets in other research. In correlation with experimental data for quinone derivatives 6-311G(d) basis set yields an intermediate EAs between 6-31++G** and DZP++ basis sets.

Overall results could be applied for validation of both computational quantum chemical methods and experimental databases for electronic energies of quinones. Besides this, the results will be helpful for evaluating redox potentials of quinones in solution.

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ЛИТЕРАТУРА
REFERENCES

1. **Bachman J.E., Curtiss L.A., Assary R.S.** Investigation of the redox chemistry of anthraquinone derivatives using density functional theory. *J. Phys. Chem.* A 2014. 118. P. 8852–8860. DOI: 10.1021/jp5060777.

2. **Chen F., Zhang J., Jiang H., Wan X.** Colorless to purple-red switching electrochromic anthraquinone imides with broad visible/near-IR absorptions in the radical anion state: simulation-aided molecular design. *Chemistry, an Asian J.* 2013. 8. P. 1497–1503. DOI: 10.1002/asia.201300176.
3. **Guerard J.J., Tentscher P.R., Seijo M., Samuel Arey J.** Explicit solvent simulations of the aqueous oxidation potential and reorganization energy for neutral molecules: gas phase, linear solvent response, and non-linear response contributions. *Phys. Chem. Chem. Phys.* 2015. 17. P. 14811–14826. DOI: 10.1039/C4CP04760E.
4. **Imperatore C., Persico M., Aiello A., Luciano P., Guiso M., Sanasi M.F., Taramelli D., Parapini S., Cebrián-Torrejón G., Doménech-Carbó A., Fattorusso C., Menna M.** Marine inspired antiplasmodial thiazinoquinones. Synthesis, computational studies and electrochemical assays. *RSC Adv.* 2015. 5. P. 70689–70702. DOI: 10.1039/C5RA09302C.
5. **Kalimullina L.R., Nafikova E.P., Asfandiarov N.L., Chizhov Y.V., Baibulova G.S., Zhdanov E.R., Gadiev R.M.** Theoretical estimation of the electron affinity for quinone derivatives by means of density functional theory. *Russ. J. Phys. Chem.* 2015. 89. P. 429–435. DOI: 10.1134/S0036024415030152.
6. **Satheshkumar A., Ganesh K., Elango K.P.** Charge transfer facilitated direct electrophilic substitution in phenylaminonaphthoquinones. Experimental, theoretical and electrochemical studies. *New J. Chem*. 2014. 38. P. 993-1003. DOI: 10.1039/c3nj01228j.
7. **Seto K., Nakayama T., Uno B.** Formal redox potentials of organic molecules in ionic liquids on the basis of quaternary nitrogen cations as adiabatic electron affinities. *J Phys. Chem.* B. 2013. 117. P. 10834–10845. DOI: 10.1021/jp402457k.
8. **Sviatenko L.K., Gorb L., Hill F.C., Leszczynski J.** Theoretical study of ionization and one-electron oxidation potentials of N-heterocyclic compounds. *J. Computational Chem.* 2013. 34. P. 1094–1100. DOI: 10.1002/jcc.23228.
9. **Vázquez K., Espinosa-Bustos C., Soto-Delgado J., Tapia R.A., Varela J., Birriel E., Segura R., Pizarro J., Cerecetto H., González M., Paulino M., Salas C.O.** New aryloxy-quinone derivatives as potential anti-Chagasic agents. Synthesis, trypanosomicidal activity, electrochemical properties, pharmacophore elucidation and 3D-QSAR analysis. *RSC Adv*. 2015. 5. P. 65153–65166. DOI: 10.1039/C5RA10122K.
10. **Wang C., Liu H.X., Fang Z.Y., Wang Z.Y.** Density Functional Theory Calculation on Polychlorinated Anthraquinones. Their Gas Phase Thermodynamic Function and Implication of the Cl Substituted Position. *J. Chem. Eng. Data*. 2010. 55. P. 1077–1086. DOI: 10.1021/je9003564.
11. **Marenich A.V., Ho J., Coote M.L., Cramer C.J., Truhlar D.G.** Computational electrochemistry: prediction of liquid-phase reduction potentials. *Phys. Chem. Chem. Phys*. 2014. 16. P. 15068–15106. DOI: 10.1039/C4CP01572J.
12. **Lopez-Moreno A., Clemente-Tejeda D., Calbo J., Naeimi A., Bermejo F.A., Orti E., Perez E.M.** Biomimetic oxidation of pyrene and related aromatic hydrocarbons. Unexpected electron accepting abilities of pyrenequinones. *Chem. Commun*. 2014. 50. P. 9372–9375. DOI: 10.1039/C4CC04026K.
13. **Liu X.Y., Ma W., Zhou H., Cao X.M., Long Y.T.** Bridge- and solvent-mediated intramolecular electronic communications in ubiquinone-based biomolecular wires. *Scientific Reports*. 2015. 5. P. 1-11.
14. **Cherkasov A., Muratov E.N., Fourches D., Varnek A., Baskin I.I., Cronin M., Dearden J., Gramatica P., Martin Y.C., Todeschini R., Consonni V., Kuz'min V.E., Cramer R., Benigni R., Yang C., Rathman J., Terfloth L., Gasteiger J., Richard A., Tropsha A.** QSAR modeling: where have you been? Where are you going to? *J.Med. Chem.* 2014. 57. P. 4977–5010. DOI: 10.1021/jm4004285.
15. **Katritzky A.R., Karelson M., Lobanov V.S.** QSPR as a means of predicting and understanding chemical and physical properties in terms of structure. *Pure and Applied Chemistry.* 1997. 69. P. 245-248. DOI: 10.1351/pac199769020245.
16. **Katritzky A.R., Fara D.C., Petrukhin R.O., Tatham D.B., Maran U., Lomaka A., Karelson M.** The Present Utility and Future Potential for Medicinal Chemistry of QSAR/QSPR with Whole Molecule Descriptors. *Current Topic in Medicinal Chemistry.* 2002. 34. P. 1333-1356. DOI: 10.2174/1568026023392922.
17. **Baskin I.I., Ait A.O., Halberstam N.M., Palyulin V.A., Alfimov M.V., Zefirov N.S.** Application of Methodology of Artificial Neural Networks for Predicting the Properties of Sophisticated Molecular Systems: Prediction of the Long-Wave Absorption Band Position for Symmetric Cyanine Dyes. *Doklady Physical Chemistry.* 1997. 357(1-3). P. 353–355.
18. **Baskin I.I., Palyulin V.A., Zefirov N.S.** Neural networks in building QSAR models. *Methods in Molecular Biology*. 2008. 458. P. 137–158.
19. **Tetko I.V.** Neural Network Studies. 4. Introduction to Associative Neural Networks. *J. Chem. Inf. Comput. Sci.* 2002. 42. P. 717–728. DOI: 10.1021/ci010379o.
20. **Vorberg S., Tetko I.V.** Modeling the Biodegradability of Chemical Compounds Using the Online CHEmical Modeling Environment (OCHEM). *Molecular Informatics*. 2014. 33. P. 73–85. DOI: 10.1002/minf.201300030.
21. **Puzyn T., Leszczynski J., Cronin M.T.D.** Recent Advances in QSAR Studies: Methods and Applications (Challenges and Advances in Computational Chemistry and Physics, 8). Springer Science+Business Media B.V. 2010.
22. **Pineda Flores S.D., Martin-Noble G.C., Phillips R.L., Schrier J.** Bio-Inspired Electroactive Organic Molecules for Aqueous Redox Flow Batteries. 1. Thiophenoquinones. *J. Phys. Chem.* C 2015. 119. P. 21800–21809. DOI: 10.1021/acs.jpcc.5b05346.
23. **Er S., Suh C., Marshak M.P., Aspuru-Guzik A.** Computational design of molecules for an all-quinone redox flow battery. *Chem. Sci.* 6 (2015) 885–893. DOI: 10.1039/C4SC03030C.
24. **Huskinson B., Marshak M.P., Suh C., Er S., Gerhardt M.R., Galvin C.J., Chen X., Aspuru-Guzik A., Gordon R.G., Aziz M.J.** A metal-free organic-inorganic aqueous flow battery. *Nature.* 2014. 505. P. 195–198. DOI: 10.1038/nature12909.
25. **Chen E.C.M., Wentworth W.E.** A comparison of experimental determinations of electron affinities of pi charge transfer complex acceptors. *J. Chem. Phys.* 1975. 63. P. 3183-3191. DOI: 10.1063/1.431807.
26. **Hilal S.H., Carreira L.A., Karickhoff S.W., Melton C.M.** Estimation of Electron Affinity Based on Structure Activity Relationships. *Quant. Struct.-Act. Relat.* 1993. 12. P. 389–396. DOI: 10.1002/qsar.19930120407.
27. **Fukuda E.K., McIver R.T.** Relative electron affinities of substituted benzophenones, nitrobenzenes, and quinines. *J. Am. Chem. Soc.* 1985. 107. P. 2291–2296. DOI: 10.1021/ja00294a014.
28. **Gurvich L.V., Vedeneyev V., Kondrat'yev V.N., Medvedev V.A., Vedeneyev Y.L.** Bond energies, ionization potentials and electron affinities. New York: St. Martins Press. 1966.
29. **Frontana C., A´lvaro V.-M., Garza J., Vargas R., Ignacio G.** Substituent Effect on a Family of Quinones in Aprotic Solvents: An Experimental and Theoretical Approach. *J. Phys. Chem.* A. 2006. 110. P. 9411–9419. DOI: 10.1021/jp060836+.
30. **Zhu X.Q., Wang C.H.** Accurate estimation of the one-electron reduction potentials of various substituted quinones in

DMSO and CH_3CN. *J. Org. Chem*. 2010. 75. P. 5037–5047. DOI: 10.1021/jo100735s.

31. **Anouar E.H., Osman C.P., Weber J.-F.F., Ismail N.H.** UV/Visible spectra of a series of natural and synthesised anthraquinones: experimental and quantum chemical approaches. SpringerPlus. 2014. 3. P. 1-12. DOI: 10.1186/2193-1801-3-233.
32. **Bradbury S.P., Mekenyan O., Veith G.D., Zaharieva N.** SAR Models for Futile Metabolism. One-Electron Reduction of Quinones, Phenols and Nitrobenzenes. *SAR and QSAR in Environmental Research*. 1995. 4. P. 109–124. DOI: 10.1080/10629369508029908.
33. **Kim K.C., Liu T., Lee S.W., Jang S.S.** First-Principles Density Functional Theory Modeling of Li Binding: Thermodynamics and Redox Properties of Quinone Derivatives for Lithium-Ion Batteries. *J. Am. Chem. Soc*. 2016. 138. P. 2374–2382. DOI: 10.1021/jacs.5b13279.
34. **Evans D.H.** One-electron and two-electron transfers in electrochemistry and homogeneous solution reactions. *Chem. Rev*. 2008. 108. P. 2113–2144. DOI: 10.1021/cr068066l.
35. **Eberle B., Hubner O., Ziesak A., Kaifer E., Himmel H.-J.** What Makes a Strong Organic Electron Donor (or Acceptor)? *Chemistry*. 2015. 21. P. 8578–8590. DOI: 10.1002/chem.201406597.
36. **Miranda-Quintana R.A., Martinez Gonzalez M., Ayers P.W.** Electronegativity and redox reactions. *Phys. Chem. Chem. Phys*. 2016. 18. P. 1-23. DOI: 10.1039/C6CP03213C.
37. **Zhan C.G., Nichols J.A., Dixon D.A.** Ionization Potential, Electron Affinity, Electronegativity, Hardness, and Electron Excitation Energy. Molecular Properties from Density Functional Theory Orbital Energies. *J. Phys. Chem*. A. 2003. 107. P. 4184–4195. DOI: 10.1021/jp0225774.
38. **Parker V.D.** Energetics of Electrode Reactions. Ⅱ. The Relationship between Redox Potentials. Ionization Potentials, Electron Affinties, and Solvation Energies of Aromatic Hydrocarbons. *J. Am. Chem. Soc*. 1976. 1. P. 98–103.
39. **Merkel P.B., Luo P., Dinnocenzo J.P., Farid S.** Accurate oxidation potentials of benzene and biphenyl derivatives via electron-transfer equilibria and transient kinetics. *J. Org. Chem*. 2009. 74. P. 5163–5173. DOI: 10.1021/jo9011267.
40. **Winget P., Weber E.J., Cramer C.J., Truhlar D.G.** Computational electrochemistry. Aqueous one-electron oxidation potentials for substituted anilines. *Phys. Chem. Chem. Phys*. 2000. 2. P. 1231–1239. DOI: 10.1039/a909076b.
41. **Tabner B.J., Yandle J.R.** A Correlation of Half-wave Reduction Potentials with Theoretical Calculations for Some Nitrogen-containing Heteromolecules in Dimethylformamide. *J. Chem. Soc*. (A) 1968. P. 381–388. DOI: 10.1039/j19680000381.
42. **Nau W.M., Adam W., Klapstein D., Sahin C., Walter H.** Correlation of Oxidation and Ionization Potentials for Azoalkanes. *J. Org. Chem*. 1997. 62. P. 5128–5132. DOI: 10.1021/jo970574v.
43. **Davis A.P., Fry A.J.** Experimental and computed absolute redox potentials of polycyclic aromatic hydrocarbons are highly linearly correlated over a wide range of structures and potentials. *J. Phys. Chem*. A. 2010. 114. P. 12299–12304. DOI: 10.1021/jp106088n.
44. **Griffith O.L., Anthony J.E., Jones A.G., Shu Y., Lichtenberger D.L.** Substituent effects on the electronic characteristics of pentacene derivatives for organic electronic devices: dioxolane-substituted pentacene derivatives with triisopropylsilylethynyl functional groups. *J. Am. Chem. Soc*. 2012. 134. P. 14185–14194. DOI: 10.1021/ja3056672.
45. **Ruzié C., Karpinska J., Laurent A., Sanguinet L., Hunter S., Anthopoulos T.D., Lemaur V., Cornil J., Kennedy A.R., Fenwick O., Samorì P., Schweicher G., Chattopadhyay B., Geerts Y.H.** Design, synthesis, chemical stability, packing, cyclic voltammetry, ionisation potential, and charge transport of [1]benzothieno[3,2-b][1]benzothiophene derivatives. *J. Mater. Chem*. C. 2016. 4. P. 4863–4879. DOI: 10.1039/C6TC01409G.
46. **Yokota Y., Mino Y., Kanai Y., Utsunomiya T., Imanishi A., Wolak M.A., Schlaf R., Fukui K.-I.** Comparative Studies of Photoelectron Spectroscopy and Voltammetry of Ferrocene-Terminated Self-Assembled Monolayers Possessing Different Electron-Donating Abilities. *J. Phys. Chem*. C. 2014. 118. P. 10936–10943. DOI: 10.1021/jp5023899.
47. Chemaxon JChem. www.chemaxon.com/jchem.
48. **Becke A.D.** Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys*. 1993. 98. P. 5648. DOI: 10.1063/1.464913.
49. **Olcari L.** Ab initio molecular orbital theory. *Inorg. Chim. Acta*. 1986. 119. P. 234. DOI: 10.1016/S0020-1693(00)84345-5.
50. **Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Mennucci B., Petersson G.A., Nakatsuji H., Caricato M., Li X., Hratchian H.P., Izmaylov A.F., Bloino J., Zheng G., Sonnenberg J.L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery Jr. J. A., Peralta J.E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Rega N., Millam J.M., Klene M., Knox J.E., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Martin R.L., Morokuma K., Zakrzewski V.G., Voth G.A., Salvador P., Dannenberg J.J., Dapprich S., Daniels A.D., Farkas Ö., Foresman J.B., Ortiz J.V., Cioslowski J. Fox, D.J.** Gaussian 09. Revision A02. Gaussian, Inc. Wallingford CT. 2009.
51. **Su N.Q., Zhang I.Y., Wu J., Xu X.** Calculations of ionization energies and electron affinities for atoms and molecules. A comparative study with different methods. *Front. Chem. China*. 2011. 6. P. 269–279. DOI: 10.1007/s11458-011-0256-3.

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