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THEORETICAL INVESTIGATION OF 2,6-DIFLUORO-4-NITROANILINE WITH SEMI-EMPIRICAL LEVELS OF THEORY

Abstract. In this work quantum chemical approach was applied in order to investigate the electronic structure and certain properties of 2,6-difluoro-4-nitroaniline with a series of semi-empirical methods using the GAMESS software. Protic and aprotic Polarized Continuum solvent models were used to study the influence of the media to the electronic structure and geometry of the molecule. It has been found that calculations using solvent models make possibility to obtain more accurate results than for vacuum. The comparison of calculated results with the available XRD crystallographic data shows that all obtained values are within acceptable deviations.

Keywords: computational research, 2,6-difluoro-4-nitroaniline, theoretical study, semi-empirical calculations, quantum chemistry.

Introduction. Aromatic amines are of great importance in the life and material sciences as well as in the pharmaceutical and chemical industries. Due to the wide use of all aromatic amines, halogenated anilines have become the most important. They are widely used as dyes, pesticides, anesthetics, surfactants and reagents for chemical synthesis including production of polymers [1].

Amino group play a crucial role in most interactions of anilines with different substrates. It can be modified by N-H-bond fictionalization using Ullmann [2], Buchwald-Hartwig [3,4] or Chan-Evans-Lam protocols [5,6] to produce a wide range of derivatives. Therefore, extensive experimental and theoretical investigations have been focused on the structure and properties of aniline and its derivatives.

In modern theoretical scientific research, the quantum chemical approach issued to extend the experimental studies and search for good theoretical parameters to characterize or explain the experimental results. Quantum chemical calculations are indispensable method to view inside the molecule and investigate the features of its electronic structures. On the other hand, computational methods allow the prediction of the variety of practically important properties of substances and complex systems according to electronic density, charge distribution or other descriptors. The electronic structure of compounds has traditionally been studied using methods based on density functional theory (DFT). Nevertheless, this approach is still extremely computationally demanding, and sometimes may not be practical for many systems of interest [7]. Semi-empirical methods are much faster and therefore have great potential to provide acceptable results. Greater speed comes at the expense of approximations made in evaluating the integrals describing

interactions between the nuclei and some integrals of the electrons (considered negligible) are ignored while others are estimated from experiments [8].

Semi-empirical calculations used very often for theoretical investigations of anilines. Some hydrogen-bonded complexes between 2,5-dihydroxy-3,6-dichlorobenzoquinone and anilines in the crystalline form were investigated by Habeeb and Gohar by FTIR spectroscopy and AM1 semi-empirical calculations[9]. Semi-empirical approach to aniline oligomers hyperpolarizabilities were performed by Machado *et al.* at the AM1/TDHF level of theory [10]. Klein *et al.* investigated of N-H-bond dissociation enthalpies and ionization potentials of substituted anilines using DFT and semi-empirical PM3 and AM1 quantum chemical methods [11]. Kumer *et al.* investigated aniline and nitrobenzene with computational overview [12]. Non-substituted 4-nitroaniline have been theoretically studied by Kavitha [13]. Comparison of quantum chemical parameters and Hummett constants in correlation with pK_a values of substituted anilines was performed by Seybold *et al* [14]. Zhou calculated the molecular descriptors of anilines with semi-empirical AM1 method to predict their carcinogenicity [15].

The objective of our research is 2,6-difluoro-4-nitroaniline (2.6-DFNA). The choice is because this compound is the first and unstudied in a series of important derivatives of 4-nitroaniline with a similar structure. Structural formula and atomic enumeration for 2.6-DFNA, adopted in this study are given in Fig.1.

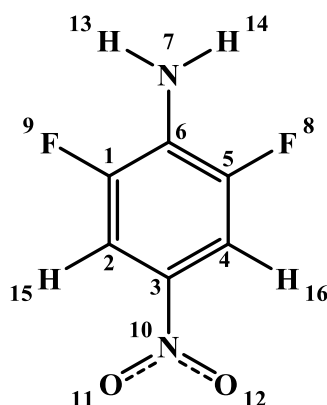


Figure 1. Molecular model of 2.6-DFNA with atomic enumeration adopted in this study

This substance has a set of useful properties and find the practical applications in a wide range of areas. Sydnese used 2,6-DFNA in attempt to synthesize photodegradable antimicrobial agent[16]. Xi *et al.* designed and synthesized N-phenyl- γ -lactam derivatives possessing two covalently identical *ortho*-F nuclei on the N-phenyl group to study no covalent interactions between F and amide or CH_2 groups. One of them was synthesized from 2,6-DFNA [17].

Investigation was performed using MNDO, AM1 and PM3 levels of theory. Semi-empirical methods are differ in the details of the approximations and were developed to reproduce heats of formation and structures of organic molecules. The selected methods have already proven their effectiveness in studying properties of similar compounds [18].

Computational details. All calculations in the present work are performed using the personal computer Intel(R) Core(TM) i7-4510U CPU (2.60 GHz and 4Gb RAM) with GAMESS [19] software program for Windows OS. For initial geometry clean up molecular modelling was performed by Avogadro software [20]. Results of the computations were visualized with Jmol program package [21]. The molecular geometry was fully optimized without any constraint using the analytical gradient procedure implemented in the program package. The computational study was carried out for gaseous and solution phase. Water and dimethylsulfoxide (DMSO) as polar protic and polar aprotic solvent media were used to include the solvent effect. For better approach of the experimental results in solution phase, Tomasi's Polarized Continuum Model (PCM) was used.

To characterize the 2.6-DFNA structure the following quantum chemical descriptors were estimated;

- 1) the energy of the highest occupied molecular orbital HOMO (eV);
- 2) the energy of the lowest unoccupied molecular orbital LUMO (eV);
- 3) energy gap (ΔE_{gap}): $\Delta E_{\text{gap}} = E_{\text{HOMO}} - E_{\text{LUMO}}$
- 4) dipole moment (μ),
- 5) ionization potential (IP), $\text{IP} = -E_{\text{HOMO}}$
- 6) electron affinity (EA), $\text{EA} = -E_{\text{LUMO}}$
- 7) global hardness (η), $\eta = \frac{I - A}{2}$
- 8) global softness (σ), $\sigma = \frac{1}{\eta}$
- 9) electronegativity (χ) $\chi = \frac{I + A}{2}$

Geometries were preliminary optimized using MM+ force field. Then structures were re-optimized by the MNDO, AM1 or PM1 levels of theory. HOMO-LUMO energies were used to obtain energy gap (ΔE_{gap}) values and to calculate the global reactivity descriptors in accordance with equations 3-9 given above. The only available X-ray diffraction data of 3,5-difluoro-4-nitroaniline published by Martin²² were used to assess the accuracy of the calculated data.

Results and its discussions.

Optimized geometry.

Fig. 2 presents the planar and unconstrained optimized geometries of 2.6-DFNA obtained at the benchmark semi-empirical levels of theory for gaseous and various solvent models.

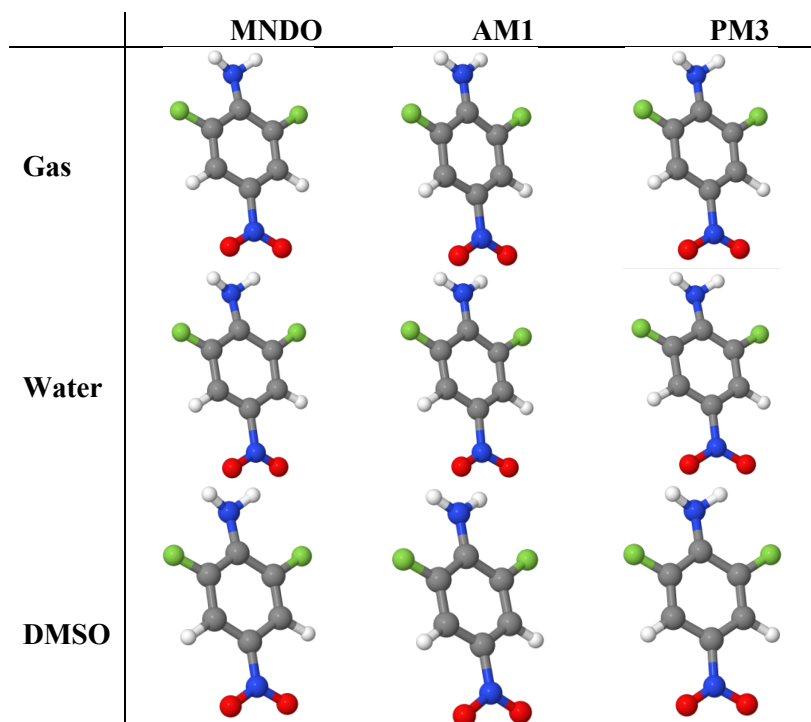


Figure 2. Molecular structure of 2,6-difluoro-4-nitroaniline optimized by different semi empirical methods for gaseous state and solvent models

Geometry optimization showed that molecule shape of 2,6-DFNA obtained by AM1 level of theory is planar in gaseous and solution state. The torsion angles are equal to 180° , which determines the planar configuration of the molecule corresponds to C_{2v} space group. This is in agreement with the available experimental data. Nevertheless, it is known that the amino group in aniline and its derivatives has a pyramidal geometry. The interaction of the amino group of aniline with the substituent on the ring is of great importance in determining its properties. Application of other methods and solvent models, gave angular structures. Hydrogen atoms and difluoro-4-nitroaniline moiety joined to nitrogen atom forms trigonal pyramidal shape similar to other most ammonia derivatives.

The optimized structural parameters like bond lengths and bond angles for the thermodynamically preferred geometry of 2,6-DFNA are presented in tables below, in accordance with the atom numbering shown in Fig.1.

Bond length. Calculated values of bond length of 2,6-DFNA in comparison with experimental data are listed in Table 1.

Table 1
Bond lengths (nm) of 2,6-DFNA calculated for different solvent models by semi-empirical methods

Atom 1	Atom 2	Experiment	MNDO			AM1			PM3		
			Gas	H ₂ O	DMSO	Gas	H ₂ O	DMSO	Gas	H ₂ O	DMSO
C1	C2	1.4116	1.3849	1.4163	1.3731	1.4260	1.4417	1.3791	1.3021	1.3253	1.3123
C2	C3	1.4108	1.3562	1.4346	1.3222	1.3777	1.3906	1.3812	1.3208	1.3491	1.3192
C3	C4	1.4108	1.4705	1.3488	1.3377	1.4593	1.3615	1.3774	1.3649	1.3846	1.4156
C4	C5	1.3695	1.2652	1.4483	1.3564	1.3710	1.5164	1.3852	1.4103	1.3074	1.2800

C5	C6	1.4116	1.3128	1.4525	1.4112	1.4205	1.4629	1.3982	1.3546	1.3289	1.3119
C1	F9	1.3399	1.3805	1.4185	1.1612	1.3969	1.3859	1.4804	1.4018	1.3844	1.3157
C5	F8	1.3399	1.3335	1.3214	1.3531	1.3421	1.3462	1.3315	1.3166	1.2820	1.3587
C6	N7	1.3443	1.4502	1.2887	1.3011	1.3533	1.3358	1.3502	1.3086	1.3875	1.3388
C2	H15	0.9726	1.2956	1.4113	1.3516	1.3199	1.4267	1.4124	1.3212	1.2281	1.3116
C4	H16	0.9726	0.9547	0.9319	1.1640	1.1741	1.1440	1.1022	0.9927	1.0153	1.2150
N7	H13	0.8676	1.0874	1.1816	1.1268	1.1088	1.1546	1.1199	1.1171	1.0998	1.0690
N7	H14	0.8676	1.1054	1.0260	1.0823	1.0099	0.9761	1.0164	1.0273	1.0404	1.0537
C3	N10	1.4308	0.9882	0.9631	1.0273	1.0505	0.9488	0.9446	1.0555	1.0848	1.0052
N10	O11	1.2320	1.1800	1.5215	1.2057	1.5716	1.4490	1.5122	1.1661	1.2280	1.2262
N10	O12	1.2320	1.4151	1.0165	1.4746	1.1525	1.2898	1.2348	1.4292	1.3371	1.3313

As can be seen from Table 1, calculations obtained for water-solvent model gave higher values of bond lengths by each methods than for gaseous and DMSO-models. The results of calculations using water-solvent model turned out to be the closest to the experimental ones. At the same time, the results of the calculation by the MNDO method turned out to be the most accurate. Calculations by the PM3 method gave the least consistent result. Evidently, the agreement between theoretical and experimental data is very good.

Bond angles

Calculated values of bond angles of 2,6-DFNA molecule are given in Table 2.

Table 2

Values of bond angles of 2,6-DFNA calculated for different solvent models by semi-empirical methods

Atom 1	Atom 2	Atom 3	Experiment	MNDO			AMI			PM3		
				Gas	H ₂ O	DMSO	Gas	H ₂ O	DMSO	Gas	H ₂ O	DMSO
C6	C1	F9	121.51	121.17	118.19	123.64	120.26	121.26	121.53	118.12	117.35	121.66
C2	C1	F9	121.51	116.76	118.79	117.04	118.20	115.46	119.46	125.06	125.42	121.36
C2	C1	C6	123.41	122.07	123.02	119.07	121.53	123.28	119.00	116.81	117.14	116.97
C1	C2	C3	119.68	118.76	115.40	121.73	122.18	119.45	126.15	127.28	122.29	126.17
C1	C2	H15	116.50	117.56	119.23	118.67	119.32	120.46	116.05	113.43	114.52	115.27
H15	C2	C3	120.09	123.68	125.38	119.60	118.49	120.08	117.78	119.29	123.19	118.49
C2	C3	N10	122.43	127.40	114.55	126.04	120.71	123.13	123.39	129.59	123.33	126.12
C2	C3	C4	115.14	117.55	122.99	116.25	117.53	120.42	116.97	114.09	118.84	115.70
C3	N10	O11	118.97	115.96	121.70	119.31	117.52	120.14	119.60	119.05	119.35	120.05
C3	N10	O12	118.97	132.28	111.88	127.92	112.68	123.61	119.73	128.83	127.98	125.06
O11	N10	O12	122.06	111.75	126.40	112.63	127.23	116.25	120.66	112.10	112.64	114.80
N10	C3	C4	122.43	115.04	122.45	117.70	121.77	116.44	119.63	116.32	117.80	118.17
C3	C4	H16	120.09	117.28	126.86	124.54	123.98	128.22	123.87	122.19	123.98	119.90
C3	C4	C5	123.41	117.81	123.34	123.87	118.14	122.45	117.51	125.67	119.16	115.46
C5	C4	H16	116.50	124.91	109.79	111.58	117.87	109.29	118.62	112.13	116.83	124.62
C4	C5	F8	118.79	117.01	122.50	122.82	117.16	122.81	117.94	124.28	118.69	114.73
C4	C5	C6	119.68	127.91	114.85	111.92	125.64	115.70	129.66	113.13	121.58	127.09
C6	C5	F8	121.51	115.09	122.66	125.21	117.18	121.47	112.28	122.59	119.71	118.17

C5	C6	C1	118.67	115.91	120.41	126.80	114.95	118.69	110.63	123.00	120.94	118.57
C5	C6	N7	120.66	121.84	116.05	109.97	126.33	117.62	127.55	115.65	122.86	118.68
C6	N7	H13	121.25	112.83	118.12	112.13	122.56	120.13	113.50	119.07	124.09	114.52
C6	N7	H14	121.25	121.00	123.61	125.10	119.31	121.26	112.38	121.17	118.29	123.09
H13	N7	H14	117.50	126.17	118.27	122.73	112.37	113.27	110.79	119.76	117.61	122.36
C1	C6	N7	120.66	122.26	123.54	122.74	118.52	123.48	121.07	121.35	116.16	122.75

From Table 2 it can be observed that the best agreement for bond angles calculations was obtained using the AM1 method with water-solvent model. Calculations performed for the gas phase with at MNDO level of theory gave a slightly less agreement. Bond angle values were found to be almost similar with minor differences. On the other hand, using other methods leads to deviations that are more significant from the available experimental results.

Mulliken charge population analysis. The local reactivity of 2,6-DFNA molecule was investigated using Mulliken charge population analysis, which is an indicator of the nucleophilic and electrophonic centers of the molecule. The molecule regions with high electronic charge are chemically softer than the regions with low electronic charge. Mulliken charges distribution in 2,6-DFNA molecule investigated in this work are listed in Table 3.

Table 3

Mulliken charge distribution in 2,6-DFNA molecule calculated for different solvent models by semi-empirical methods

Atom	MNDO			AM1			PM3		
	Gas	H ₂ O	DMSO	Gas	H ₂ O	DMSO	Gas	H ₂ O	DMSO
C1	-0.0331	0.0845	0.0582	-0.0214	0.0459	0.0616	-0.0127	-0.1054	-0.0527
C2	0.1603	0.0114	0.0735	-0.0802	-0.0839	-0.1234	0.0163	0.0681	0.0203
C3	-0.1487	-0.1633	-0.0530	-0.1550	-0.0787	-0.0802	-0.3581	-0.4585	-0.4404
C4	0.0505	0.0301	-0.0568	-0.0646	-0.1024	-0.0833	0.0040	0.0445	0.0061
C5	0.0477	0.0587	0.0986	0.0164	0.0203	0.0474	-0.0756	-0.0891	-0.0401
C6	0.2163	0.1357	0.1628	0.1030	0.0743	0.0136	-0.0274	-0.0094	-0.0052
N7	-0.2917	-0.3666	-0.3814	-0.3406	-0.3699	-0.2602	0.1709	0.2528	0.1749
F8	-0.2291	-0.1464	-0.1452	-0.1087	-0.0692	-0.1095	-0.0491	-0.0974	-0.0923
F9	-0.1788	-0.1758	-0.1830	-0.0978	-0.0910	-0.0800	-0.0609	-0.0523	-0.0796
N10	0.4268	0.5770	0.3550	0.5839	0.5188	0.5353	1.1541	1.2329	1.2416
O11	-0.4417	-0.1672	-0.3808	-0.2980	-0.3855	-0.3398	-0.6453	-0.6512	-0.6404
O12	-0.3021	-0.4994	-0.2622	-0.3872	-0.3113	-0.3421	-0.5889	-0.6209	-0.6176
H13	0.2516	0.2030	0.2185	0.2425	0.2193	0.2014	0.0828	0.0953	0.0853
H14	0.2398	0.2087	0.2398	0.2339	0.2208	0.1877	0.0984	0.0858	0.0954
H15	0.1024	0.0876	0.1389	0.1847	0.2012	0.1756	0.1342	0.1412	0.1735
H16	0.1298	0.1219	0.1171	0.1891	0.1912	0.1961	0.1575	0.1637	0.1712

The basic properties of the molecule can be estimated from the partial charge of the nitrogen atoms of the amino group. The lower the charge on the corresponding atoms, the higher the ability of the molecule to attach a proton i.e. act as the Lewis base. Calculations by the MNDO and AM1 methods gave similar values of the partial nitrogen atomic charge. Application of the PM3 method showed the presence of a positive charge on the nitrogen atom of amino group. This indicates a very low basicity of the studied molecule, even in comparison with unsubstituted aniline, where the calculated charge on the same atom is -0.9030.

The orbital provides information about electron density, which in turn is used to determine which part of the molecule participates most actively in an energy transfer event. The energy of the HOMO is directly related to the ionization potential (IP), the LUMO energy is directly related to the electron

affinity (EA). The energy difference between the HOMO and LUMO orbital is called the energy gap, which is an important stability factor for the compound, meaning that the molecule with the smallest HOMO-LUMO gap is more reactive. The computed quantum chemical parameters like HOMO-LUMO, ΔE_{gap} energies of 2,6-DFNA molecule and global chemical reactivity descriptors calculated with equations 3-9 by semi empirical methods for different states are summarized in Table 4.

Table 4

Quantum chemical descriptors of 2,6-DFNA

Descriptor	MNDO			AMI			PM3		
	Gas	H ₂ O	DMSO	Gas	H ₂ O	DMSO	Gas	H ₂ O	DMSO
ΔH_f° , kcal/mol	-48.8045	-49.0864	-48.6453	-64.3083	-64.3189	-64.2716	-71.5050	-71.3112	-71.3778
μ , D	8.6740	5.5120	6.9560	5.8630	5.9510	5.3830	10.7690	6.7010	9.4270
E_{HOMO} , eV	-1.1646	-1.1374	-1.1673	-0.7456	-0.4190	-0.8435	-0.7020	-0.7102	-0.7428
E_{LUMO} , eV	-0.2231	-0.2476	-0.0327	-0.4544	-0.0520	-0.0816	-0.6694	-0.7156	-0.6966
ΔE_{gap} , eV	1.3877	1.3850	1.2000	1.2000	0.4710	0.9251	1.3714	1.4258	1.4394
EA, eV	-0.2231	-0.2436	-0.0327	-0.4544	-0.0520	-0.0816	-0.6694	-0.7156	-0.6966
IP, eV	1.1646	1.1374	1.1673	0.7456	0.4190	0.8435	0.7020	0.7102	0.7428
η , eV	-0.6939	-0.6925	-0.6000	-0.6000	-0.2355	-0.4626	-0.6857	-0.7129	-0.7197
σ_r , eV	-1.4412	-1.4441	-1.1667	-1.6667	-4.2462	-2.1618	-1.4584	-1.4027	-1.3895
χ_r , eV	0.4707	0.4449	0.5673	0.1456	0.1835	0.3809	0.0136	0.0027	0.0231

Independently from the calculation model used, PM3 method predicts the lowest value of the heat of formation and MNDO - the highest. In any case, it means that the molecule of 2,6 - DFNA is stable. Calculations show that taking into account the influence of the solvent leads to a lower value of the dipole moment of the molecule than in vacuum. Electronegativity values indicates the solubility of 2,6 – DFNA in highly polar solvents.

Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the major orbital's involved in chemical stability. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to receive an electron. The HOMO is the highest energy MO containing electrons. The electrons in these molecular orbital can be donated to the LUMO-type molecular orbital. This is because these molecular orbital contain weakly bound electrons. These molecular orbital are the most available form for covalent chemical bonds. The presence of these molecular orbital is characteristic of nucleophiles. HOMO has low energy. Therefore, electrons tend to stay in these molecular orbital; because electrons try to fill the low energy levels first. HOMO-LUMO values are negative, indicating that lower excited states are still bound systems or that the electron-rich 2,6-DFNA molecule is stable with excess electrons. The LUMO is the lowest energy orbital capable of accepting electrons and therefore acts as an electron acceptor and characterizes the vulnerability of the molecule to attack by nucleophiles. Values of E_{LUMO} are negative close to zero that indicates that 2,6-DFNA is weak electrophile.

It is clearly known that hard molecule with a large energy gap, and a soft molecule has a small gap. Positive value of energy gap (greater than 1.0 eV) means that 2,6-DFNA is a hard molecule. A negative HOMO/LUMO gap should not be possible for ground states - the unoccupied orbital is always higher in energy than the occupied one. If such result was obtained, it means either the simulation depicts an excited (and thus unstable) state or the optimization method used is unsuitable for the given system.

The rare discrepancies between the theoretical predictions and the experimental results are due to the effect of the solvent which allow to the

conformational distribution can greatly alter the magnitude of the nonlinear response²⁴.

Conclusion. The aim of the present work was to investigate 2,6-difluoro-4-nitroaniline in gaseous and solution phases. Quantum-chemical calculations were performed with the series of fundamental semi-empirical methods and were used for comparison with the available experimental results. The polar solvent environment turned out to be the best model for predicting the geometry of the molecule. Research has shown that 2,6-DFNA is stable as an electron-rich molecule due to the excess of electrons and also negative value of the heat of formation. It was also found that 2,6-DFNA is a hard molecule with weak basic properties that could be soluble in polar solvents. Our calculations demonstrated that all theoretical data agreed well with the available experimental data. The results of this investigation complement those of previous studies for similar systems.

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ТЕОРИЯНЫҢ ЖАРТЫЛАЙ ЭМПИРИКАЛЫҚ ДЕҢГЕЙІНДЕ 2,6-ДИФТОР-4-НИТРОАНИЛИНДІ ТЕОРИЯЛЫҚ ЗЕРТТЕУ

Аңдатпа. Жұмыста GAMESS бағдарламалық құралын және жартылай-эмпирикалық әдістерді пайдаланып, 2,6-дифтор-4-нитроанилиннің электрондық құрылымын, кейбір қасиеттерін зерттеу үшін кванттық химиялық тәсіл қолданылды. Молекуланың электрондық құрылымы мен геометриясына орталардың әсерін зерттеу үшін поляризацияланған континуумды еріткіштердің протонды жән еапротонды үлгілері пайдаланылды. Еріткіш үлгілерді қолданатын есептеулер вакуумға қарағанда жоғары нәтиже беретіні анықталды. Есептелген

нәтижелерді қолжетімді кристаллографиялық деректерімен салыстыру барлық алынған мәндердің тұрақтыш егінде екенін көрсетеді.

Тірек сөздер: кванттық химиялық есептеулері, 2,6-дифтор-4-нитроанилин, теориялық зерттеу, жартылай эмпирикалық есептеулер, кванттық химия.

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ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ 2,6-ДИФТОР-4-НИТРОАНИЛИНА НА ПОЛУЭМПИРИЧЕСКОМ УРОВНЕ ТЕОРИИ

Аннотация. В работе квантово-химический подход применен с целью исследования электронной структуры и некоторых свойств 2,6-дифтор-4-нитроанилина с помощью полуэмпирических методов с использованием программного обеспечения GAMESS. Протонные и апротонные модели растворителей (модели поляризованного континуума) использовались для изучения влияния сред на электронную структуру и геометрию молекулы. Установлено, что расчеты с использованием выбранных моделей растворителей позволяют получить более точные результаты, чем для вакуума. Сравнение расчетных результатов с имеющимися кристаллографическими данными показывает, что все полученные значения находятся в пределах допустимых отклонений.

Ключевые слова: квантохимические расчёты 2,6-дифтор-4-нитроанилин, теоретическое исследование, полуэмпирические расчеты, квантовая химия.