The European Journal of Technical and Natural Sciences 2025, No 2
ISSN 2414-2352

PREMIER Publishing
ppublishing.org

Section 1. Chemistry

DOI:10.29013/EJTNS-25-2-3-7

QUANTUM-CHEMICAL STUDY OF THE ELECTRONIC STRUCTURE AND REACTIVITY OF REAGENTS FOR THE SYNTHESIS OF 2- METHYL –2-(A-PHENYL AMINO) PROPANE NITRILE

Mamarakhmonov Mukhamatdin [1], Qodrov Abduahad [2], Rustamov Sardor [2], Izbasarova Gulnoza [2], Khamraeva Komila [2], Adumutalova Farog'at [3], Mamarakhmonov Nasrulloh [4]

[1] Department Mathematics&Informatics, Andijan State Pedagogical Institute

[2] Department of Organic Chemistry, Qarshi State University

[3] Departent Chemistry, Andijan State Universty

[4] Cybersecurity faculty, Tashkent Information Technology University

Cite: *Mamarakhmonov M., Qodrov A., Rustamov S., Izbasarova G., Khamraeva K., Adumutalova F., Mamarakhmonov N. (2025). Quantum-chemical study of the electronic structure and reactivity of reagents for the synthesis of 2- methyl -2-(α-phenyl amino) propane nitrile. European Journal of Technical and Natural Sciences 2025, No 1.* https://doi.org/10.29013/EJTNS-25-2-3-7

Abstract

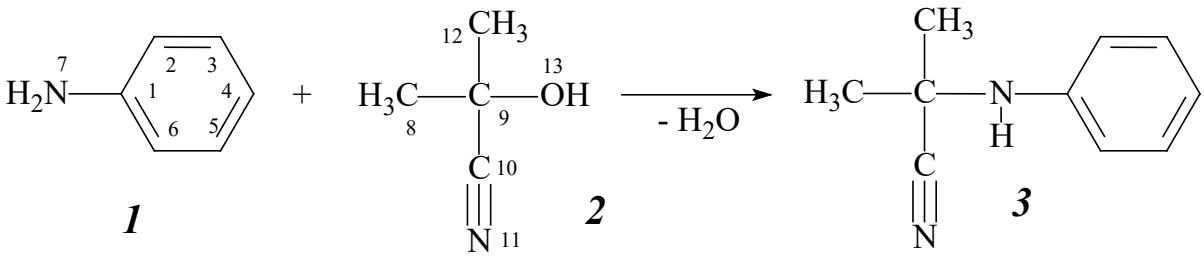
Organic synthesis is a rapidly developing main branch of scientific research in chemistry, the derivatives of which serve as a medicinal, preparative base for medicine, agriculture at the present stage of development and everyday activity of human activity. It should be noted that some non-benzene aromatic compounds with high biological activity are synthesized on the basis of α-aminonitrile derivatives. The solution to the problem of establishing the reactivity of reagents and the synthesis route depending on the electronic structure of α-aminonitrile derivatives is easily amenable to using theoretical methods. This article is devoted to the quantum-chemical study of the synthesis of 2-methyl-2-(α-phenylamino) propanenitrile by the modern DFT method using the Gaussian98 program. For further study of the true reactivity, the reaction route and the scientific substantiation of the mechanism of electrophilic substitution reactions, in our opinion, the theoretical data we obtained, the wise thoughts of mentors and logical conclusions will be very useful.
Keywords: *2-methyl-2-(α-phenylamino) propanenitrile, nonbenzoic aromatic compounds, organic synthesis, quantum chemical calculation, DFT B3LYP method, Gaussian98, electronic structure, reactivity, nuclear reaction control, frontier molecular orbitals, biological activity, medicine, pharmacology, agriculture*

Introduction

Organic synthesis undoubtedly makes a significant contribution to the development of chemical sciences, depending on the multitude of aromatic and acyclic derivatives of synthesis with high biological activity. Numerous experimental studies are also devoted to the synthesis of α-aminonitrile derivatives (Yurovskaya M. A., Kurkin A. V., Lukashev N. V. 2007; Allen J. M., Lambert T. H. J. 2011; Nauth A. M. 2017), widely used in pharmaceuticals, medicine, agriculture and animal husbandry (Belen'kii L.I., 2020; Grundke C. 2023; Severin E. S. 2003).

This article is devoted to a theoretical study of the synthesis of 2-methyl-2(α-phenylamino) propanenitrile, the scheme of which is presented below:

Figure 1. *Scheme of synthesis of 2-methyl 2(phenylamino) propanitrile (numbering is arbitrary)*



Experimental

A 100 ml round-bottomed two-necked flask was equipped with a magnetic stirrer, a separatory funnel at one end, and a Dean-Stark trap filled with hexane, and a reflux condenser at the other end. 5g (5.38 ml, 0.058 mol, d = 0.93 g / ml) of hexane were added to the flask, then acetone cyanohydrin was added and 5.4 g (0.058 mol, 5.3 ml, d = = 1.02 g/ml) of aniline were added dropwise through a separatory funnel, while the reaction mixture was boiling. The reaction mixture was boiled for two hours. Then the reaction mixture was extracted with chloroform and 2/3 of the solvent was removed. The resulting white precipitate was filtered and recrystallized from hexane. As a result, 5.4 g (58%) of the reaction product were obtained. The melting point of the obtained substance is $t_{m.p.}$ = 78–79 °C, R_f = 0.34 (acetone: benzene – 1:2).

Method

In order to study the route of synthesis of compound ***3***, to identify the reactivity of reagents ***1***, ***2,*** as well as changes in the charges on the atoms and orbital density of the intermediates – molecular ions ***1a***, ***2a.*** We carried out quantum chemical calculations using the Gaussian program using the DFT method B3LYP (Frisch M. J.F., 1998), successfully used in the past (Mamarakhmonov M. Kh., 2024; Chuliyev Zh.R., Qodirov A. A., Mamarakhmonov M.Kh., 2020). The results of which are presented in Table 1.

Results

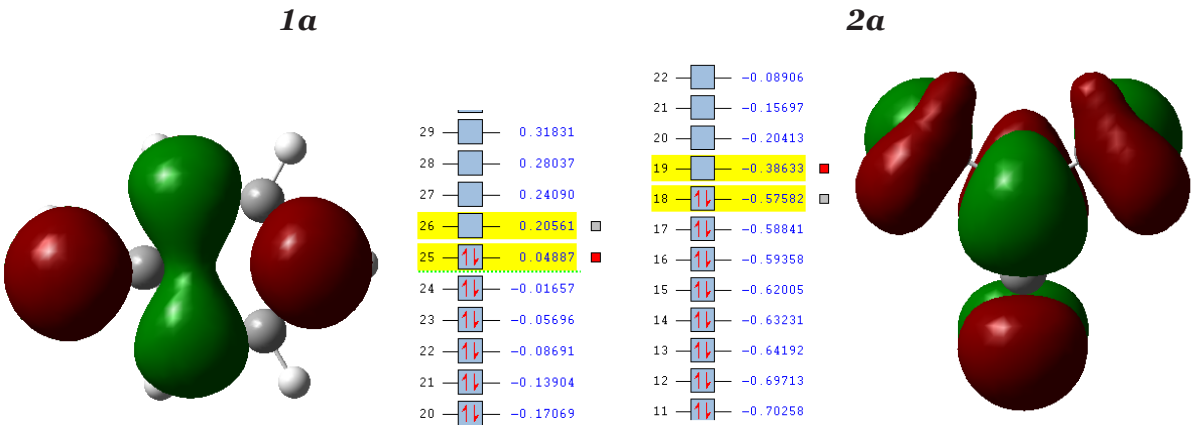
Geometrical parameters of compounds. *Bond lengths*. In the aromatic ring of aniline ***1***, symmetry in bond lengths relative to the **C1-C4** axis can be observed. In this case, the **C1-C2** and **C6-C1** bond lengths are adjacent and are equal to d = 1.41Å, while the **C2-C3** and **C3-C4** bonds are respectively equal to 1.39Å and 1.40Å. The length of the exocyclic bond **C1- N7** is equal to d = 1.38Å. After the deprotonation process and the formation of the molecular anion ***1a,*** a noticeable elongation in bonds **C1-C2** (Δd =0.045Å) and shortening of the bond **C1-N7** (Δd = 0.045Å. When the hydroxyl anion is eliminated from compound ***2*** and transformed into the molecular cation ***2a***, the **C8-C9**, **C9-C10**, **C9-C12** bonds are shortened by Δd = 0.075Å, 0.066Å, 0.075Å, respectively, and the C10≡N11 triple bond is lengthened by almost

0.01Å. *Bond angles*. On the aromatic ring of the molecular anion of aniline ***1,*** both bond angles **C1-C2-C3** and **C5-C6-C1** decrease by Δφ=2.245°; the **C3-C4-C5** angle increases by Δφ=2.301°. The exocyclic valence angles **C6-C1-N7** and **C1-N7-H** decrease by Δφ=1.293° and 12.688°, respectively. In compound ***2***, upon transition to molecular cation ***2a,*** the value of the valence angles **C8-C9-C10** and **C8-C9-C12** increases accordingly on Δφ=8.820° and 11.513°, forming an almost symmetrical *sp2* – hybridized form. *Torsion angles*. In the aromatic ring of aniline ***1***, all torsion angles remain unchanged. In compound ***2,*** the torsion angles **C8-C9-C10-N11** and **N11-C10-C9-C12** synchronously increase by Δτ=27.377°, upon transition to molecular cation ***2a***.

Charges on atoms. In the aromatic ring of compound ***1***, by removing a proton, the negative charge on atoms **C2**, **C3**, **C4**, **C5** increases by Δq = –0.029e, –0.012e, –0.049e, –0.019e, than at the positively charged atom **C1**, in which the magnitude of the positive charge decreases by Δq = +0.129e. The exocyclic atom **N7** passes into *the sp3* – hybrid form; the negative electron charge is equal to q = – 0.079e and this atom becomes a potential reaction center for electrophilic attack. Compound ***2*** with the elimination of the hydroxyl anion passes into the molecular cation ***2a***, on the atoms of which a redistribution of the electron charge occurs. If the negative charge decreases by atom **N11** (Δq = –0.172e), then the negative charge on the atoms **C8**, **C12**, symmetrically located relative to the axis **N11-C9**, increases synchronously by Δq = –0.095e. The positive charge on the atoms **C9**, **C10** decreases by Δq = +0.054e, +0.010e, respectively. According to the tabular data, the atoms **C8** and **C12** in compound ***2a*** carry the maximum negative charge q = –0.622e and are a potential center of reactivity under charge control.

Boundary molecular orbitals. The picture below of the electron densities of the reagents in the stage of activated complexes ***1a***, ***2a*** (Fig. 2) makes it possible to estimate the centers of potential reactivity in reactions controlled by orbitals. In the molecular anion ***1a***, a high contribution of the **N7** atom is observed. on the HOMO, emphasizing it as a center of reactivity. In the molecular cation ***2a***, the unsaturated, *sp* – hybridized atom **C9** has a high contribution to the LUMO, emphasizing it as the only center of reactivity, rather than the atoms **C8**, **C12**.

Figure 2. *Orbital electron densities: left – **1a**; right – **2a***



Discussion

In the synthesis of compound **3**, the determining stage of the reaction path is the process of formation of activated complexes ***1a*** and ***2a***. Analysis of the geometry of molecular ions and the redistribution of electron charges on atoms, as well as the orbital picture of the boundary orbitals led to an identical conclusion that the potential reaction centers of compounds ***1a***, ***2a*** are atoms **N7** and **C9**, respectively. Therefore, the synthesis of compound ***3,*** in our opinion, occurs with the active participation of the latter.

Table 1. *Geometrical parameters and charge distribution on reactant atoms*

Atom	Charge, q, e				Bonds	Length, d, Å				Bond angle, φ	degree			
	1	1 a	2	2 a		1	1 a	2	2 a		1	1a	2	2a
C 1	0.335	0.206			**C1-C2**	1.411	1.456			**C1-C2-C3**	120.852	123.097		
C 2	−0.198	−0.227			**C2-C3**	1.392	1.387			**C3-C4-C5**	118.725	117.051		
C3	−0.189	−0.201			**C3-C4**	1.397	1.405			**C5-C6-C1**	120.883	123.184		
C4	−0.204	−0.253			**C4-C5**	1.397	1.412			**C6-C1-N7**	121.118	119.825		
C5	−0.185	−0.204			**C5-C6**	1.392	1.381			**C1-C2-H**	119.220	117.546		
C6	−0.198	−0.188			**C6-C1**	1.411	1.456			**C1-N7-H**	120.862	108.174		
N7	−0.831	−0.752			**C1-N7**	1.378	1.333			**C8-C9-C10**			109.597	118.417
C8			−0.527	−0.622	**C2-H**	1.085	1.090			**C9-C10-N11**			179.379	179.959
C9			0.041	0.187	**C3-H**	1.085	1.091			**C8-C9-C12**			111.603	123.116
C10			0.422	0.412	**C4-H**	1.083	1.085			**C8-C9-O13**			110.736	
N11			−0.472	−0.300	**C5-H**	1.085	1.091			**C9-C8-H**			109.173	112.753
C12			−0.527	−0.622	**C6-H**	1.085	1.086			**C9-C12-H**			109.173	112.753
O13			−0.524		**N7-H**	1.011	1.048			**C9-O13-H**			106.106	
H 2	0.164	0.088			**C8-C9**			1.543	1.468	**Torsion angle, τ**	1	1a	2	2a
H 3	0.179	0.098			**C9-C10**			1.469	1.403	**C1-C2-C3-C4**	0.002	−0.001		
H 4	0.172	0.085			**C10-N11**			1.163	1.172	**C4-C5-C6-C1**	0.001	0.000		
H 5	0.179	0.099			**C9-C12**			1.543	1.468	**C3-C2-C1-N7**	179,999	179.998		
H 6	0.164	0.109			**C9-O13**			1.468		**C1-C2-C3-H**	180.00	179.999		
H7	0.303	0.139			**C8-H**			1.096	1.090	**C8-C9-C10-N11**			61.396	88.773
H8			0.226	0.303	**C12-H**			1.096	1.090	**N11-C10-C9-C12**			61.396	88.773
H12			0.226	0.303	**O13-H**			0.997		**N11-C10-C9-O13**			180.00	
H13			0.340							**C8-C9-C12-H**			57.795	−16.270
										C8-C9-O13-H			−62.176	
										C12-C9-C8-H			−57.795	16.270

References

Yurovskaya M. A., Kurkin A. V., Lukashev N. V. Chemistry of aromatic heterocyclic compounds / – M. 2007.
Allen J. M., Lambert T. H. *J. Am. Chem. Soc.* 2011. – 133. – P. 1260–1262.
Nauth A. M. etc. / *Eur. J. Org. Chem.* 2017. – P. 6966–6974.
Belen'kii L.I. etc. / The literature of heterocyclic chemistry. Part XX, 2020. – 10.1016/bs.aihch.2022.10.005, (201–274), (2023).
Grundke C. etc. / Complementary Mechanochemical and Biphasic Approaches for the Synthesis of Organic Thiocyanates using Hexacyanoferrates as Non-Toxic Cyanide Sources. – Org. Biomol. Chem., 2023. – 21. – P. 644–650.
Severin E. S. Biochemistry: Textbook for universities / – M.: GEOTAR – Media. 2003. – 779 p.
Frisch M. J.F. and etc. Gaussian 98, Revision A. 5, Gaussian Inc. – Pittsburgh (PA), 1998.
Mamarakhmonov M. Kh. et. al. Quantum-chemical study of the electronic structure and reactivity of 2-phenyl-2-(α-tolyl-amino) acetonitrile // Universum: technical sciences: electronic. scientific journal. 2024. – 12(129). URL: *https://7universum.com/ru/tech/archive/item/18928/ (Accessed 07.02.2025)*.
Chuliyev Zh. R., Qodirov A. A., Mamarakhmonov M. Kh., et al. Synthesis, crystal structure of mono- and bis α-aminonitriles and classification based on chemical composition / Austrian Journal of Technical and Natural Sciences. – No. 9–10. 2020. – P. 47–52.

submitted 21.01.2025;
accepted for publication 05.02.2025;
published 26.12.2024

Contact: muhamatdin@mail.ru; kodirov.aa@qarshidu.uz