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STANDARD ENTHALPIES OF FORMATION IN THE GAS PHASE AND RELATIVE STABILITY OF TAUTOMERS OF C-NITRO-1,2,4-TRIAZOLE AND ISOMERS OF N-ALKYL-C-NITRO-1,2,4-TRIAZOLE: QUANTUM-CHEMICAL STUDIES*

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Quantum-chemical calculations of the standard enthalpies of formation in the gas phase of C-nitro-1,2,4-triazole and isomers of N-alkyl-C-nitro-1,2,4-triazoles (Alk = Me, Et, i-Pr, t-Bu) were carried out by the B3LYP method using equations for the isodesmic reactions and isomerization reactions. The relative Gibbs free energies of tautomers and isomers in aqueous solution were calculated. For the tautomers of C-nitro-1,2,4-triazole the structural indexes of aromaticity were estimated and the electron population density of the Natural Bond Orbital was analyzed. The relative stabilities of the described tautomers and isomers in the gas phase and in solutions were discussed on the basis of the results of the calculations.

Keywords: C-nitro-1,2,4-triazole, isomerism, quantum-chemical calculations, B3YLP method, standard enthalpies of formation.

Five-membered polynitrogen heterocycles are effective components of composite propellants, pyrotechnic, explosive, and gas-generating compositions [1, 2]. In this area nitrotriazoles are of especial interest, and also their substituted derivatives and triazolium salts which are characterized by a unique complex of properties – high energy consumption with considerable thermal stability and high nitrogen content. Apart from this, the 1,2,4-triazole ring is found in the composition of a substantial number of medicinals [3]. In this connection a real problem is the development of new and improved known methods of synthesis of derivatives of 1,2,4-triazole, in particular N-alkyl-C-nitrotriazoles and their salts.

One of the methods of obtaining these compounds is alkylation of the corresponding C-nitrotriazoles, but this is complicated by the presence of several reactive centers for electrophilic agents – the nitrogen atoms of the heterocycle in the subrate molecules [4-7]. For predicting the ratio of the isomers formed during

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* Dedicated to Academician B. A. Trofimov in his 70th jubilee.

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functionalization of the ring and the development of methods for the selective synthesis of the certain isomers information about relative stability of isomeric N-substituted compounds under various conditions is of essential interest. In addition, in connection with the possible use of derivatives of 1,2,4-triazole as components of combustible and thermally destructive systems, it is of particular value to determine enthalpies of formation of these substances.

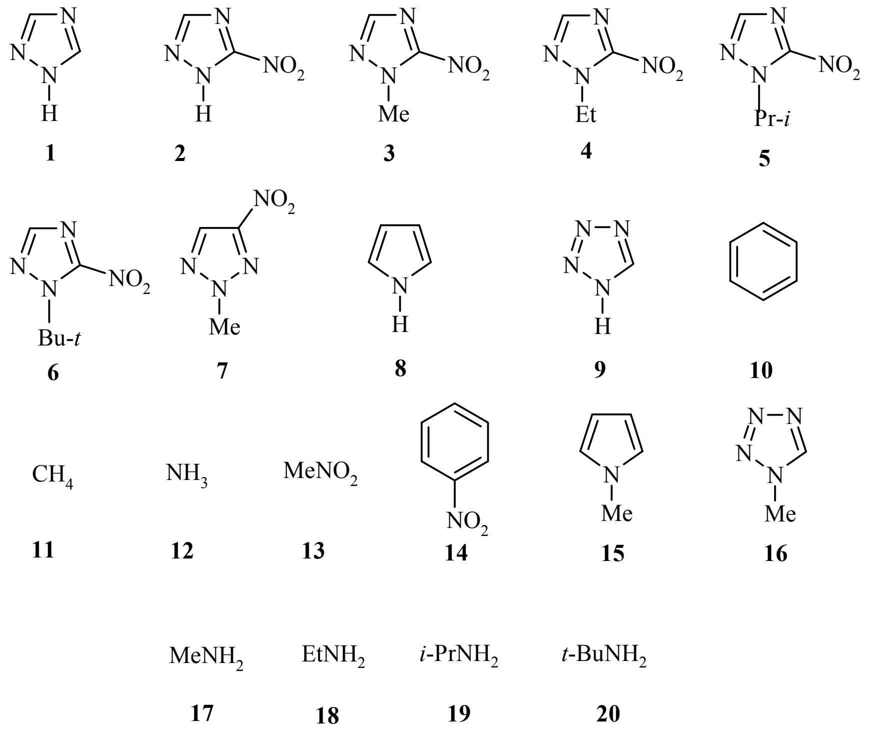
The experimental study of these properties of azoles in a number of cases is restricted by the high sensitivity of these substances to friction, shock, and heat, the possibility of isomerization, prototropic tautomerization and other specifics. Thus among triazoles the enthalpy of formation in the gas phase has been determined experimentally up to now only for unsubstituted 1,2,4-triazole [8, 9].

At the same time there are a number of publications concerned with quantum-chemical calculation of the enthalpy of formation of unsubstituted 1,2,3- and 1,2,4-triazoles [10-12], 4-nitro- and 4,5-dinitro-1-2,3-triazoles [13], and some substituted 1,2,4-triazolium salts [14]. Tautomerism of unsubstituted 1,2,4-triazole [15-24] and some of its C- and N-substituted derivatives [25-28] have been studied by various physicochemical and quantum-chemical methods. However, the influence of the solvents on the relative stability of the tautomeric forms of C-nitro-1,2,4-triazole has not been studied previously. Analogous data for the isomeric N-alkyl-2-nitro-1,2,4-triazoles in the gas phase and in solutions are absent from the literature.

Previously we have calculated the relative stability of the tautomers of C-nitro-1,2,3-triazole and the isomers of N-alkyl-C-nitro-1,2,3-triazole in the gas phase and in solutions [29] and their enthalpies of formation in the gas phase [30]. The data obtained permit the explanation of the results of the experimental investigation of the alkylation of 1,2,3-triazoles in acidic and basic solutions and of C-nitro-1,2,3-triazole with diethyl sulfate [29].

In the present work we have carried out quantum-chemical calculations of the standard enthalpies of formation in the gas phase of the tautomers of C-nitro-1,2,4-triazole and the isomers of N-alkyl-C-nitro-1,2,4-triazoles (Alk = Me, Et, *i*-Pr, *t*-Bu) using the equations for the isodesmic and isomerization reactions. The

Scheme 1



relative Gibbs energies of the tautomers and isomers in aqueous solution have been calculated. For the tautomers of C-nitro-1,2,4-trazole the calculated indexes of aromaticity have been compared with the corresponding characteristics of the tautomers of C-nitro-1,2,3-triazole and tetrazole. The relative stabilities of the tautomers in the gas phase and in solution are discussed.

The standard enthalpies of formation of 1H-5-nitro-1,2,4-triazole and 1-alkyl-5-nitro-1,2,4-triazoles in the gas phase have been calculated starting from the calculated values of the standard enthalpies of the isodesmic reactions. The enthalpy of formation of 1-methyl-5-nitro-1,2,4-triazole was also obtained from the calculated value of the enthalpy of isomerization 2-methyl-4-nitro-1,2,3-triazole → 1-methyl-5-nitro-1,2,4-triazole and the experimental value of $\Delta_f H^\circ_{298}$(g) for 2-methyl-4-nitro-1,2,3-triazole [30]. We note that the latter reaction is not isodesmic: for example, the C–C bond which was present in the starting material is absent from the product.

The structures of the molecules of the C-nitro-1,2,4-triazoles studied and compounds used in this work to construct the equations of the isodesmic and isomerization reactions are cited in Scheme 1 and the experimental values of their standard enthalpies of formation are given in Table 1. The enthalpies of formation of 1H-3-nitro- and 4H-3-nitrotautomers and the corresponding N-alkyl-substituted compounds were calculated starting from the calculated values of the standard enthalpies of isomerization and the values of $\Delta_f H^\circ_{298}$ (g) for 1H-5-nitro- and 1-alkyl-5-nitro-1,2,4-nitrotriazoles. We have shown the effectiveness of this approach for the examples of derivatives of C-nitro-1,2,3-triazole [30]. For example, the calculated value $\Delta_f H^\circ_{298}$ (g) for 2-methyl-4-nitro-1,2,3-triazole obtained in [30] (233.5 k/mol) is in excellent agreement with the experimental value (228.7 ± 3.5 kJ/mol) [30].

Schemes of the isodesmic and isomerization reactions used to calculate $\Delta_f H^\circ_{298}$(g) for 1H-nitro- and 1-alkyl-5-nitro-1,2,4-triazoles and the corresponding calculated values for the standard enthalpies are shown in Table 2. For aromatic compounds it is important not only to retain the number of chemical bonds in each form in the isodesmic reaction but also the aromatic unit. Fulfilling the latter conditions we chose 1H-1,2,4-triazole as standard compound and set up the schemes of the isodesmic reactions so that the 1,2,4-triazole fragment was not destroyed during the reaction.

Six isodesmic reactions and one isomerization reaction were examined for 1-methyl-5-nitro-1,2,4-triazole. The enthalpies of formation of the remaining C-nitro-1,2,4-triazoles were calculated on the basis of two isodesmic reactions. For 1-methyl-5-nitro-1,2,4-triazole a strong difference exists in the enthalpies of formation calculated with the first and fourth schemes for the isodesmic reactions: the enthalpy of formation in the first of these was 17.9 kJ/mol smaller than in the fourth (Table 2).

This difference is explained by errors in the calculated and experimental values of the enthalpies of formation of pyrrole, N-methylpyrrole, methane, nitromethane, 1H-tetrazole, 1-methyltetrazole, benzene, and nitrobenzene.

Table 1. Standard Enthalpies of Formation of Standard Compounds in the Gas Phase Used in the Schemes for the Isodesmic and Isomerization Reactions

Compound	$\Delta_f H^\circ_{298}$,(g) kJ/mol	Reference	Compound	$\Delta_f H^\circ_{298}$,(g) kJ/mol	Reference
1	192.9 ± 0.8	[8]	**14**	65.77 ± 0.42	[37]
7	228.7 ± 3.5	[30]	**15**	103.1 ± 0.54	[38]
8	108.3 ± 0.50	[31]	**16**	322.9 ± 2.0	[39]
9	334.3 ± 4.2	[32]	**17**	-22.50	[40]
10	82.93 ± 0.50	[33]	**18**	-47.50	[40]
11	-74.85 ± 0.31	[34]	**19**	-83.7 ± 0.8	[41]
12	-45.90	[35]	**20**	-120.0 ± 0.8	[41]
13	-81.0 ± 1.0	[36]			

Table 2. Schemes of Isodesmic and Isomerization Reactions for 1H-5-Nitro- and 1-Alkyl-5-nitro-1,2,4-triazoles and Calculated Values of the Standard Enthalpies of Reaction ($\Delta_r H°_{298}$) and Formation ($\Delta_f H°_{298}$) in the Gas Phase

Compound	Reaction scheme	$\Delta_r H°_{298}$, kJ/mol	$\Delta_f H°_{298}$,kJ/mol
2	**1 + 13 = 2 + 11**	15.2	202.0
	1 + 14 = 2 + 10	36.0	211.7
3	**1 + 13 + 15 = 3 + 11 + 8**	7.3	188.9
	1 + 13 + 16 = 3 + 11 + 9	21.7	197.0
	1 + 14 + 15 = 3 + 10 + 8	28.1	198.6
	1 + 14 + 16 = 3 + 10 + 9	42.4	206.8
	1 + 13 + 17 = 3 + 11 + 12	-15.8	194.3
	1 + 14 + 17 = 3 + 10 + 12	5.0	204.1
	7 = 3	-34.0	194.7
4	**1 + 13 + 18 = 4 + 11 + 12**	-11.1	174.1
	1 + 14 + 18 = 4 + 10 + 12	9.7	183.9
5	**1 + 13 + 19 = 5 + 11 + 12**	-10.9	138.1
	1 + 14 + 19 = 5 + 10 + 12	9.9	147.8
6	**1 + 13 + 19 = 6 + 11 + 12**	10.9	123.5
	1 + 14 + 19 = 6 + 10 + 12	31.6	133.3

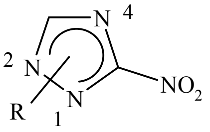
One of the shortcomings of the isodesmic reactions method is that calculation of the enthalpy of formation of compounds requires experimental values of formation of the standard substances. At present reliable experimental data are not available for all of the standard substances. In addition, errors arise in calculating the heat effects of the isodesmic reactions. Finding an average value for the range of enthalpies of formation calculated for all the isodesmic reactions used for the given compound, permits the partial compensation of the errors caused by the characteristics of the concrete isodesmic reactions.

The calculated average values for 1H-5-nitro-1,2,4-triazole and 1-alkyl-5-nitro-1,2,4-triazoles are given in Table 3 (taking into account the isomerization reaction for 1-methyl-5-nitro-1,2,4-triazole). We note that the value of the enthalpy of formation of 1-methyl-5-nitro-1,2,4-triazole calculated from the isomerization scheme (194.7 kJ/mol) is in excellent agreement with the average value (198.3 kJ/mol) calculated from the schemes of isodesmic reactions (Table 2). So the use of the essentially different approachs leads to close results, which indicates the correctness of using these methods.

The calculated enthalpies of formation for the tautomeric forms of C-nitro-1,2,4-triazole are somewhat higher than for 1H-1,2,4-triazole (Tables 1 and 3). The enthalpies of formation of 1-alkyl-3-nitro-1,2,4-trazoles (N(2)-isomers) decrease with increasing number of carbon atoms in the alkyl substituent (by 25-35 kJ/mol on increasing the number of carbon atoms by one). For 1-alkyl-5-nitro- and 4-alkyl-3-nitro-1,2,4-triazole N(1)- and N(4)-isomers on going from methyl to ethyl and from isopropyl to *tert*-butyl derivatives enthalpy of formation decreases by only 19 and 15 kJ/mol respectively (Table 3) which is probably caused by the increase in steric repulsion with increasing volume of the substituent. The change in the enthalpy of formation depending on the nature and position on the ring of the alkyl substituent is in good agreement with that for N-alkyl-C-nitro-1,2,3-triazoles [30]. The N(1)- and N(2)-tautomeric forms of C-nitro-1,2,4-triazole are characterized by close values of their enthalpies of formation, whereas it is 20 kJ/mol higher for the N(4)-forms (Table 3).

These results are in good agreement with the calculated total energies (CCSD(T)/6-311++G**//B3LYP/6-311++G** and CCSD(T)/6-311++G**//B3PW91/6-311++G**) and the Gibbs energies (B3LYP/6-311++G** and B3PW91/6-311++G**) for the tautomers of C-nitro-1,2,4-triazole [28]. For the isomers of N-alkyl-C-nitro-1,2,4-triazole the N(4)-isomers are the least stable, however with increasing volume of the alkyl substituent the N(2)-isomers become noticeably more stable than the corresponding N(1)-derivatives. For example for the isomeric *tert*-butyl-C-nitro-1,2,4-triazoles the enthalpy of formation of the N(1)-isomer is more than 30 kJ/mol greater in comparison with the N(2)-derivative (Table 3). The

Table 3. Calculated Values of the Standard Enthalpies of Formation ($\Delta_f H°_{298}$) and Isomerization ($\Delta_r H°_{298}$) in the Gas Phase and the Relative Gibbs Energy in Aqueous Solution (ΔG_s) for the Tautomers of C-Nitro-1,2,4-triazole and the Isomers of N-Alkyl-C-nitro-1,2,4-triazole



R and its position in the ring	$\Delta_r H°_{298}$, kJ/mol	$\Delta_f H°_{298}$, kJ/mol	ΔG_s, kJ/mol
H(1)	0.0	206.8	0.0
H(2)	1.9	208.7	-20.8
H(4)	24.5	231.3	4.6
CH_3(1)	0.0	197.8	0.0
CH_3(2)	-7.6	190.2	--26.4
CH_3(4)	33.0	230.8	12.5
C_2H_5(1)	0.0	179.0	0.0
C_2H_5(2)	-13.9	165.1	-30.6
C_2H_5(4)	33.3	212.2	12.3
i-C_3H_7(1)	0.0	143.0	0.0
i-C_3H_7(2)	-13.2	129.8	-31.2
i-C_3H_7(4)	35.2	178.2	13.1
t-C_4H_9(1)	0.0	128.4	0.0
t-C_4H_9(2)	-30.9	97.5	-49.0
t-C_4H_9(4)	34.4	162.8	11.8

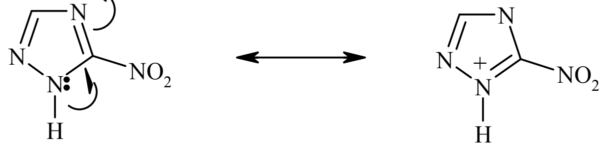
N(2)-tautomers of C-nitro-1,2,4-triazole and the N(2)-isomers of N-alkyl-C-nitro-1,2,4-triazoles are more polar than the corresponding N(1) compounds. For example, the calculated values of the dipole moments of the N(1)-, N(2)-, and N(4)-tautomers of C-Nitro-1,2,4-triazole are equal to 2.93, 7.21, and 5.63 D respectively, therefore the N(2)-tautomer is more stable in aqueous solution than its N(1)-analog (Table 3). As in the gas phase, the N(2)-isomers are the most stable in aqueous solution (Table 3).

The concept of aromaticity is frequently used for the characteristics of the structures of the molecules, their physical properties and reactivity from thermodynamic or kinetic positions [42-47]. At present there are many criteria of aromaticity. These criteria can be conditionally divided into three groups: magnetic, structural, and energetic. In addition, it is proposed to analyze the NBO (Natural Bond Orbital) on studying the degree of π-electron delocalization and aromaticity (electronic criteria) (48).

In the present work we used for the tautomeric forms of C-nitro-1,2,4-triazole, C-nitro-1,2,3-triazole, and C-nitrotetrazole structural indexes of aromaticity (the HOMA index – Harmonic Oscillator Model of Aromaticity [49], index *A,* proposed by Pozharskii [50], the I_5 index, proposed by Bird [51, 52], and the parameter Δ, which in approximation of NBO characterizes the degree of delocalization of the π-electrons and can be used as an electronic criterion of aromaticity: $\Delta = 2 - n_{p_z}$, where n_{p_z} is the occupancy of the p_z-orbitals of the pyrrole nitrogen atom.

Really, in the molecules of the heterocycles studied two of the six π-electrons of the cyclic systems (Hückel's rule) exist as an "unshared electron pair" of the heteroatom. As an example, two resonance structures for the 1H-5-nitro-1,2,4-triazole molecule are shown in Scheme 2.

Scheme 2



In the absence of a notable contribution of the resonance structures with separated charges the molecule will not be aromatic since the N(1)–N(2) and N(1)–C(5) bonds will be single bonds. Then the occupancy of the p_z orbital of atom N(1) can be used as to estimate quantitatively the delocalization of the π-electrons: the larger the value of Δ, the greater the delocalization of the π-electrons.

The calculated HOMA indexes, I_5, and A for the tautomers of C-nitrotetrazole (the results of the calculations are given in Table 4) are in good agreement with those calculated elsewhere [53-55]. For all azoles studied the most stable tautomer corresponds to the maximum values of all of the indexes of aromaticity (except for the index A for C-nitro-1,2,4-triazole). So comparison of the indexes of aromaticity in some cases allows the determination of the most stable isomer.

However these factors are not always adequate. For example, the lower stability of the N(4)-tautomeric form of C-nitro-1,2,4-triazole in comparison with the N(1)- and N(2)-forms may be explained by the repulsion of the unshared pairs of atoms N(1) and N(2) in the N(4)-tautomer [28], and also the greatest stability of the N(2)-tautomers of C-nitro-1,2,3-triazole and C-nitrotetrazole. The indexes of aromaticity are not correctly used to estimate the relative thermodynamic stabilities of isomers of derivatives of 1,2,4- and 1,2,3-triazoles since they contain different types of chemical bonds (for example, the ring has a C–C bond in 1,2,3-triazoles which is absent from the 1,2,4-triazole ring).

Thus by using combined schemes of isodesmic and isomerization reactions quantum-chemical calculations of the standard enthalpies of formation in the gas phase were carried out for the tautomers of C-nitro-1,2,4-triazole and the isomers of N-alkyl-C-nitro-1,2,4-triazole (Alk = Me, Et, *i*-Pr, *t*-Bu). For 1-methyl-5-nitro-1,2,4-triazole the values, calculated using the schemes of the isodesmic reactions, agree well with the values calculated using the isomerization reaction scheme: 2-methyl-4-nitro-1,2,3-triazole → 1-methyl-5-nitro-1,2,4-triazole. The enthalpies of formation of the studied derivatives of 1,2,4-triazole are lower than those calculated for the corresponding derivatives of 1,2,3-triazole [30]. The N(1)- and N(2)-tautomeric forms of C-nitro-1,2,4-triazole are characterized by close enthalpies of formation, whereas for the isomeric N-alkyl-C-nitro-1,2,4-triazoles with increasing volume of the alkyl substituent the N(2)-isomers become noticeably more stable than the corresponding N(1)-compounds. The N(4)-tautomers and isomers are the least stable. In aqueous solutions the stability of the more polar N(2)-tautomers and isomers are increased compared with the N(1)-compounds.

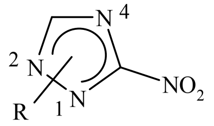
For tautomeric forms of C-nitro-1,2,4-triazole, 1,2,3-triazole, and tetrazole the indexes of aromaticity were calculated. In all the azoles studied the most stable tautomer corresponded to the maximum values of the indexes of aromaticity.

METHOD OF CALCULATION

The quantum-chemical calculations were carried out with the Gaussian-03 set of programset [56] within the realms of the functional density theory (functional B3LYP) [57]. Geometrical characteristics were calculated in the 6-31G* basis set since it gave excellent agreement with experimental values for derivatives of tetrazole [58-60]. The energy of zero vibration (ZPVE) was found for the structures obtained. The total energy (E) and dipole moments were calculated in the 6-311++G** basis set, and analysis of the electronic occupancy of the NBO was performed in the 6-311++G** basis set. The procedure for calculating the enthalpy of the isodesmic reactions ($\Delta_r H^\circ_{298}$) has been described previously [30].

The Gibbs energy taking solvation into account was calculated within the COSMO model [61], in which the molecule of the dissolved substance is placed in a hole in the solvent and the interaction between such molecules is reduced to local interactions of the virtual contacting surfaces of the dissolved molecule and the molecules of the solvent. Local interactions are determined only by the charge densities on the contacting surfaces. The optimized geometry of the isolated molecules was used in the calculations. It has been shown

Table 4. Calculated Values of the Relative Energies at 0 K ($E_0 = E + \mathrm{ZPVE}$), Bond Lengths (l) in the Ring, Structural Indexes of Aromaticity and the Values of Δ for Tautomeric Forms of the Isolated Molecules of C-Nitroazoles*



Compound	E_0, kJ/mol	l, Å					HOMA	A	I_5	Δ
		1–2	2–3	3–4	4–5	1–5				
1H-5-Nitro-1,2,4-triazole	0.0	1.345	1.334	1.360	1.313	1.348	95	74	83	0.480
2H-5-Nitro-1,2,4-triazole	1.9	1.347	1.356	1.319	1.352	1.324	95	75	83	0.462
4H-5-Nitro-1,2,4-triazole	24.5	1.373	1.320	1.359	1.362	1.308	88	58	73	0.444
1H-4- Nitro-1,2,3-triazole	0.0	1.362	1.298	1.356	1.378	1.347	91	56	73	0.483
2H-4- Nitro-1,2,3-triazole	-13.9	1.336	1.319	1.332	1.405	1.332	98	84	90	0.502
3H-4-Nitro-1,2,3-triazole	5.3	1.315	1.337	1.354	1.378	1.358	95	66	77	0.495
1H-5-Nitrotetrazole	0.0	1.341	1.303	1.358	1.310	1.344	92	66	79	0.493
2H-5-Nitrotetrazole	-11.1	1.321	1.336	1.307	1.350	1.326	98	83	90	0.524

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* The names of azoles correspond to the numbering of the bonds in the Table.

previously that this model permits a correct description of the influence of the solvent on the relative stabilities of N-substituted derivatives of tetrazole [62], tautomeric and protonated forms of tetrazole, 1,2,3-triazole and their derivatives [29, 30, 63-65]. The procedure for calculations of the relative Gibbs energies for tautomers and isomers has been described elsewhere [30].

The HOMA index of aromaticity was evaluated, starting from the bond lengths (l_i), according to the formula:

$$\mathrm{HOMA} = 100 - (100/n)\Sigma\alpha(l_{ort} - l_\mathrm{i})^2 ,$$

where n is the number of bonds in the ring (5), and α is a normalizing factor. The values of l_ort and α for various bonds are given in Table 5. The bond orders (N), needed for calculation of the aromaticity index A, were calculated from the formula:

$$N = (a/l^2) - b,$$

where l is the calculated bond length.

The values of the parameters a and b are given in Table 5. The index A is calculated from the mean value δN, the difference between all the bond orders:

$$A = 100 - (\delta \mathrm{N}/0.49)100.$$

To calculate the index of aromaticity I_5 , the degree of uniformity of the bond orders is evaluated:

$$V = \frac{100}{\bar{N}} \sqrt{\frac{\sum(N - \bar{N})}{n}} ,$$

where $\bar{N}$ is the arithmetic mean value of the bond orders. The index of aromaticity I_5 has the form:

$$I_5 = 100 - (V/35)100.$$

Table 5. Values of the Parameters l_ort, α, a, and b, Used to Calculate the Aromaticity Indexes

Bond	l_ort, Å	α	a	b
C–C	1.397	257.7	6.80	1.71
C–N	1.334	93.52	6.48	2.00
N–N	1.309	93.52	5.28	1.41

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