**DFT study of the direct electrophilic amination of aromatics**

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**Abstract**

Direct amination is an extremely valuable reaction allowing for the one-step preparation of aromatic amines. However, its’ mechanism has been poorly studied. Here, for the first time using quantum chemical calculations we have shown that direct amination of arenes by hydrazoic acid follows the classical *SEAr* mechanism with aminodiazonium cation H2N3+ (as) as electrophile. The located stationary points and transition states allowed us to define direct amination as *SEAr* reaction, which rate is determined by the early transition state between π- and σ-complexes. Considering the calculated reaction constant *ρ* we placed direct amination of arenes by HN3 somewhere in-between nitration and halogenations closer to nitration. Additionally, for the first time we have studied the acidity of hydrazoic acid and H2N3+ and calculated their p*Ka*. We have shown that an acid stronger than H2N3+ (as) with p*Ka* lower than approximately -5.32 is required for the direct amination with HN3, justifying the use of superacids or Lewis acids. Our results explain the accumulated experimental data and open a prospect for the development of the new aminating agents working in milder conditions.

**Keywords:** direct amination, density functional theory, acidity, hydrazoic acid

**Introduction**

Aromatic amines are highly valuable building blocks in fine and industrial organic synthesis. The vast majority of biologically active compounds, dyes, agrochemicals, polymers, etc. bear aromatic amino moieties 1. Usually, anilines as well as heterocyclic amines are prepared via nitration of the corresponding arene followed by the reduction of nitro group 2,3 or by other two- or multistep routes 4–8. Considering an extremely high practical importance of aromatic amines, numerous attempts have been done to directly introduce amino group into aromatics via the one-step route. For that purpose, such nitrogen-containing compounds as ammonia 9, hydroxylamine, its salts and derivatives 10–13, and hydrazoic acid (почему нет ссылки на обзор в Усп.Хим ? Обязательно !) have been used. However, ammonia and hydroxylamines showed low aminating performance. In particular, The amination of arenes with organic and inorganic azides in the presence of very strong protic or Lewis acids give slightly better results [ref]. In this case, the actual aminating agent is hydrazoic acid (HN3). However, acceptable yields in these conditions can be achieved with a limited number of aromatic substrates such as benzene and its derivatives with relatively strong electron-donating (e.g., alkylbenzenes) and electron-withdrawing (e.g. chlorobenzene) substituents.

Понимая высочайшую практическую важность ароматических аминов, химики многократно предпринимали попытки прямого одностадийного введения аминогруппы в ароматическое ядро. Для этих целей использовали некоторые типы азотсодержащих реагентов such as ammonia 9, hydroxylamine, its salts and derivatives 10–13, and hydrazoic acid (почему нет ссылки на обзор в Усп.Хим ? Обязательно !). Однако, аммиак и гидроксиламины в (условиях ? очень важно ! ) показали очень невысокую аминирующую способность в ограниченном числе случаев (каких ? развить !). Несколько лучшие результаты в аминировании некоторых аренов демонстрируют organic and inorganic azides in the presence of very strong protic acids or Lewis acids [ref]. В этих условиях истинным аминирующим агентом выступает hydrazoic acid. Однако и в этих случаях приемлемых выходов ароматических аминов удается достигнуть только с ограниченным кругом ароматических субстратов. К числу последних относятся бензол и его производные с умеренно сильными донорными (алкилбензолы) и акцепторными (хлорбензол) заместителями. Нитробензол не аминируется hydrazoic acid с практически значимыми выходами нитроанилинов. Среди бензолов с сильными электронодонорами аминируется анизол, но не анилин, причины данной закономерности ранее не обсуждались (Ксения, уточни и поправь меня). В ряду гетероаренов известно считанное число успешных методов прямого аминирования. Так N-алкилкарбазолы аминируются in 3,6-positions using by NaN3 in H2SO4 22 (выходы ???) and pyrimidine реагирует с ???, давая ???? (выход ????). Таким образом, нужно сделать вывод что до сих пор, к сожалению, не существует общего метода прямого аминирования аренов. Безусловно, это в первую очередь связано с сильно кислотными и суперкислотными условиями известных методов прямого аминирования, не являющихся толерантными к большинству желаемых ароматических субстратов. Другой причиной не слишком впечатляющих практических результатов прямого аминирования ароматических субстратов является плохое понимание возможных механизмов этих реакций. В отличие от большинства других важных реакций электрофильного ароматического замещения реакции прямого аминирования начали изучаться намного позже, и среди исследователей нет понимания не только деталей механизмов этих реакций, но даже нет единства в определении возможных принципиальных маршрутов ароматического аминирования. Вот теперь и нужно формулировать цель исследования и плавно переходить к тому, что написано ниже.

In order to broaden the range of suitable substrates and increase preparative yields the understanding of mechanism of direct amination with hydrazoic acid and its derivatives is necessary. According to the current knowledge, direct amination with HN3 refers to electrophilic substitution reactions. It starts with the protonation of hydrazoic acid by a stronger acid giving aminodiazonium ion **1** 18 (Scheme 1). Considering previous studies, this step can be then followed by two different pathways. In the first one, the aminodiazonium cation **1** (H2N3+ (as))acts as an electrophile itself (pathway **A**), whereas in the second one it decomposes to nitrenium ion **2** (NH2+) and nitrogen (pathway **B**) (Scheme 1). In the latter case, the highly reactive nitrenium ion **2** acts as an electrophile. Considering the experimental results 16–21, it is complicated to distinguish between the pathways **A** and **B**, thus they remain equally possible.

The completely different mechanism (pathway **C**) was proposed by Aksenov et al., who aminated arenes and pyrimidine using NaN3 in the presence of polyphosphoric acid (PPA) 23. The authors proposed the formation of PPA azide, which further protonation gives two tautomeric cations. The latest undergo azocoupling with arenes forming intermediate triazenes, which hydrolysis gives the amines.



Scheme 1. Proposed mechanisms of direct electrophilic amination of arenes

Overall, there are only several hypotheses regarding the mechanism of arene direct amination.

The aim of the study is to investigate possible pathway of electrophilic amination reaction of aromatic and heterocyclic substrates in nonpolar and polar media using DFT methods and identify the opportunities and limitations.

**Methods**

All the calculations were performed in Gaussian 09 (Revision-D.01-SMP) software.

**Ab Initio Calculations**

The structures of neutral molecules, ions, sigma complexes and transition states were fully optimized with Kohn−Sham density functional theory (DFT), using global-hybrid GGA functional B3LYP and aug-cc-pVDZ basis set unless otherwise indicated. The stationary points were confirmed by harmonic frequency calculations. The transition states were characterized by imaginary vibrational mode and verified by intrinsic reaction coordinate calculation. The neutral molecules, ions, sigma complexes and transition states were solvated using conductor-like polarizable continuum model (CPCM).

**Calculation of p*Ka***

By definition, the p*Ka* of hydrazoic acid can be quantified using the following proton-transfer reaction (eq 1):

(1)

However, it is known that the formation of charged species from neural molecules is a challenging task for theoretical calculations. To conserve the number of charged species we have chosen equation 2 instead of 1 as it was done in 24:

(2)

The p*Ka* of hydrazoic acid was then calculated using the following expression 24:

(3)

The reaction shown in eq 4 was used for the p*Ka* calculation of H2N3+,

(4)

with the p*Ka* calculated according to the eq 5 24:

(5)

We have found the solvation free energy (Δ*Gsol\*)* of hydrazoic acid and H2N3+ using two different solvation models: conductor-like polarizable continuum model (CPCM) and cluster-continuum model 24,25 .

In CPCM the p*Ka* was found using the data generated by calculations at B3LYP/aug-cc-pVDZ level of theory and eqs 3 and 4. Whereas in cluster-continuum model the calculations were performed as described below.

The cluster-continuum model implies that the ion is represented as a cluster formed by the ion and an optimal number of solvent molecules, which is then solvated using a dielectric continuum. For example, for the OH- and H3O+ ions the optimum number of water molecules was shown to be three 25. Thus, in the cluster-continuum model the following reactions 6 and 7 would describe the ionization of hydrazoic acid and H2N3+, respectively 24:

(6)

(7)

The p*Ka* of hydrazoic acid and H2N3+ can be then calculated using eqs 8 and 9 24:

(8)

(9)

Using a variational principle, we have found that the optimum number of water molecules for the azide anion N3- and H2N3+ equals two. We obtained the structures of ionic clusters and neutral species by optimization at the MP2/6-311++G(2df,2p) and M11/6-311++G(2df,2p)//B3LYP/6-311++G(2df,2p) level of theory. In the second case, after performing a frequency job with Gaussian09 using M11/6-311++G(2df,2p) we took the full electronic energy of the system and added the correction to Gibbs free energy from B3LYP/6-311++G(2df,2p) calculation. The solvation free energy (Δ*Gsol\*)* of clusters and neutral molecules by the bulk solvent (water) was calculated by CPCM.

**Results and discussion**

**Structure of hydrazoic acid and related compounds**

Since the molecular geometry of hydrazoic acid is well described experimentally 26–28, we used it for the justification of the chosen level of theory. The calculated and experimental values of bond distances (angstroms) and bond angles (degrees) of HN3 are summarized in Table 1.

Table 1. Calculated and experimentally determined geometries of HN3, H2N3+ (as) (singlet, Fig. 1) and NH2+.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **HN3** | | **H2N3+ (as)** | | | | | **NH2+ (singlet)** | | | **NH2+ (triplet)** | |
| expta | calcd | | exptb | calcd | 3-21Gb | LDFb | MP4c | calcd | MP4c | | calcd |
| Bond distances, Å | | | | | | | | | | | | |
| Nα-Nβ | 1.233 | 1.245 | | 1.295 | 1.288 | 1.305 | 1.276 | - | - | - | | - |
| Nβ-Nγ | 1.121 | 1.138 | | 1.101 | 1.116 | 1.088 | 1.126 | - | - | - | | - |
| Nα-H | ≈1.02 | 1.023 | | e | 1.024 | 1.008 | 1.043 | 1.043 | 1.061 | 1.025 | | 1.043 |
| Bond angles, deg | | | | | | | | | | | | |
| Nα-Nβ-Nγ | 172.8 | 171.1 | | 175.3 | 175.7 | na | 175.2 | - | - | - | | - |
| H- Nα-Nβ | 109 | 109.9 | | 107.6 | 115.2 | na | 114.5 | - | - | - | | - |
| H- Nα-H | - | - | | 118.8 | 121.08 | na | 117.9 | 107.1 | 106.9 | 149.4 | | 154.1 |

a Data from ref. 28; b Data from ref. 29; c Data from ref. 30, calculations performed at MP4/6-311+G(3d,2p); d according to our results obtained using B3LYP/aug-cc-pVDZ; na - data not available

The lowest energy structure found for hydrazoic acid using B3LYP/aug-cc-pVDZ level of theory is in good agreement with experimentally determined one 28 (Table 1). However, absorption bands assigned to in and out of plane bending of N-N-N moiety in calculated IR spectrum of hydrazoic acid are shifted in comparison to experimental values (Table 2). It could be caused by the differences in predicted and observed values of Nα-Nβ-Nγ angle - 172.8° and 171.1°, respectively.

Table 2. Calculated and observed IR absorption bands of HN3 and H2N3+ (as).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Assignment | Frequency, cm-1 | | Assignment | Frequency, cm-1 | | |
| **HN3** | | **H2N3+ (as)** | | |
| expta | calcb | exptc | calcc | calcb |
| ν N-H | 3336 | 3372 | νas NH2 | 3280 | 3372 | 3447 |
| ν Nβ-Nγ | 2140 | 2199 | νsym NH2 | 3170 | 3248 | 3313 |
| δsciss NH | 1269 | 1258 | ν N≡N | 2318 | 2350 | 2325 |
| δ NH against linear group | 1152 | 1152 | δsciss NH2 | 1547 | 1526 | 1537 |
| δ N-N-N out of plane | 739 | 573 | δas NH2 | 1259 | 1232 | 1227 |
| δ N-N-N in plane | 658 | 511 | ν N-N | 1129 | 1190 | 1134 |
|  |  |  | δ N-N-N in plane | 530 | 516 | 501 |
|  |  |  | δwag NH2 | 489 | 479 | 319 |
|  |  |  | δ N-N-N out of plane | 418 | 429 | 376 |

a Data from ref. 28; b according to our results obtained using B3LYP/aug-cc-pVDZ level of theory (scale factor 0.97); c Data from ref. 29;

The protonated hydrazoic acid (H2N3+), that is supposed to play one of the key roles in direct amination reaction, could have symmetric (H2N3+ (s)) or asymmetric (H2N3+ (as)) structure (Fig.1). To find the lowest energy structure for both of them, we scanned the potential energy surface varying the H-N-N-N dihedral and N-N-N bond angles. The predicted H2N3+ (s) structure had *C2* symmetry, N-N-N angle of 166.8° and N-N bond distance of 1.18 Å. Whereas H2N3+ (as) structure had *Cs* symmetry with a pyramidal amino group (Fig.1), N-N-N angle of 175.7° and NH2-N bond distance of 1.288 Å, which is in agreement with experimental data and previous calculations by LDF theory 29 (Table 1). On the other hand, the calculations showed NH2-N moiety flatter than it appears, resulting in less accurate predictions of the frequency of vibrations associated with its stretching and bending (Table 2). The H2N3+ (as) has an increased Nα-Nβ distance and decreased Nβ-Nγ distance as compared to hydrazoic acid. Our calculations indicate that H2N3+ (as) is favored by 25.18 kcal/mol over H2N3+ (s), which is in agreement with the results of previous calculations at 3-31G level of theory, where energy difference was found to be 49.8 kcal/mol. The studies of the crystal structure of H2N3+ salts also proved that H2N3+ cation has asymmetric aminodiazonium structure 29.

Recall, that there are two options for aminodiazonium cation in amination reaction: it could attack aromatic ring itself or decompose to highly reactive nitrenium ion. It is known that nitrenium ion can exist in either singlet or triplet state 30 and among them the triplet state is more favorable one. Taking into account that direct amination involves the formation of nitrenium ion from aminodiazonium cation, we assumed that H2N3+ could also exist in singlet and triplet state. According to the results triplet states for both H2N3+ (s) and H2N3+ (as) are much less favourable then singlet states (Fig.1). It is interesting that the energy difference between H2N3+ (as) and H2N3+ (s) in triplet state is only 3.88 kcal/mol. Both of them are predicted to be flat with significantly decreased N-N-N angle (Fig.1). For H2N3+ (as) in triplet state structure having *C2* symmetry, N-N-N angle of 117.9° and N-N bond distance of 1.18 Å was found, whereas for H2N3+ (s) in triplet state structure having *C2V* symmetry, N-N-N angle of 126.6° and N-N bond distance of 1.27 Å was found.

The study of nitrenium ion geometry in singlet and triplet state using B3LYP/aug-cc-pVDZ level of theory predicted values of bond distances and angles close to ones calculated previously at (MP4/6-311+G(3d,2p)) 30 (Table 1), except the H-N-H angle in triplet, which is noticeably higher. The triplet state was favored by 33.14 kcal/mol over singlet state, which is in agreement with experimental value of 30.09 kcal/mol 31.

Thus, the chosen level of theory proved to be appropriate and was used for further calculations.

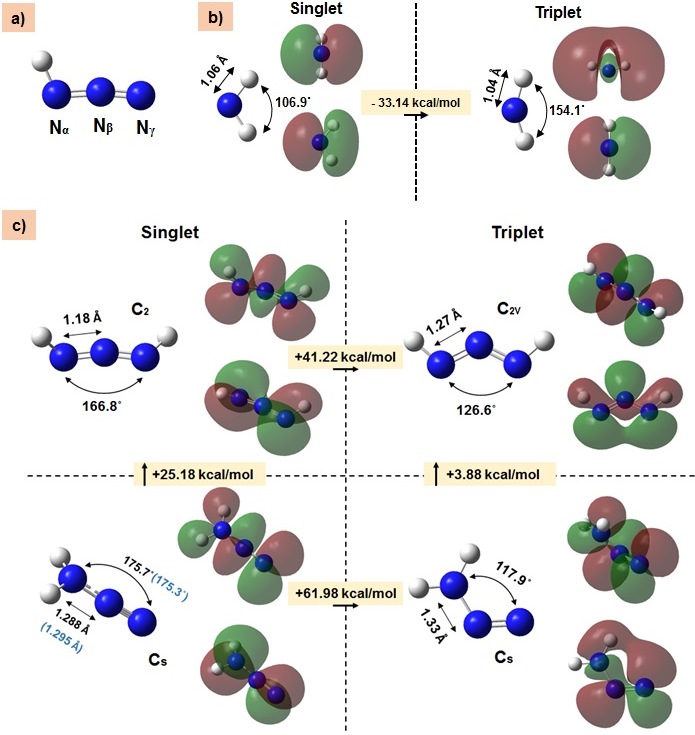


Fig.1 Structure of hydrazoic acid (a) and geometries and MO representation (LUMO above HOMO) of intermediates generated from it: b) NH2+ in singlet and triplet state and c) H2N3+ (as) and H2N3+ (s) in singlet and triplet state. The bond distances (angstroms) and bond angles (degrees) are shown according to the results of calculations at B3LYP/aug-cc-pvdz level of theory. For H2N3+ (as) experimental values are shown in blue.

**Acidity of hydrazoic acid, H2N3+ (as) and H2N3+ (s)**

Regardless of whether the direct amination proceeds with H2N3+ (as) or NH2+ as electrophile, the crucial step for these species formation is a protonation of hydrazoic acid (Scheme 1). In order to identify the conditions in which the protonation occurs, the p*Ka* of hydrazoic acid and H2N3+ are necessary. Here, for the first time we have studied the acidity of hydrazoic acid and H2N3+ and calculated their p*Ka* using both continuum and cluster-continuum solvation models.

The p*Ka* calculated for hydrazoic acid using CPCM at B3LYP/aug-cc-pvdz show poor agreement with experimental value and deviation approaching 10.6 p*Ka* units (eqs 2,3, Table 3) 32. Such a result can be explained by the general drawbacks suffered by continuum solvation models. In particular, they do not consider strong and specific interaction between solvent molecules in first coordination shell and solute. Also, continuum behavior is not observed near the solute molecules 24. Overall, it was shown that ions of organic molecules with the charge localized on nitrogen are poorly described by continuum solvation models 24,25. In this case, the better performance was achieved by using cluster-continuum solvation model, where the ion is represented as a cluster formed by the ion and an optimal number of solvent molecules, which is then solvated using a dielectric continuum. 24,25. Following this method, we built clusters formed by the ion and an optimal number of solvent molecules for all the charged species and calculated p*Ka* values (eqs 6-9, Table 3). For the OH- and H3O+ ions the optimum number of water molecules was previously shown to be three 25. Using a variational principle, we have found that the optimum number of water molecules for the azide anion N3- and H2N3+ equals two.

Table 3. Predicted and experimental p*Ka* values of hydrazoic acid and H2N3+ species.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Compound** | **Experimental** | **CPCMa** | **Cluster-continuum**  **modelb** | **Cluster-continuum**  **modelc** |
| HN3 | 4.92 32 | -5.65 | 1.89 | 4.39 |
| H2N3+ (as) | - | 3.88 | -7.85 | -5.32 |
| H2N3+ (s) | - | -10.91 | -18.15 | -17.45 |

a B3LYP/aug-cc-pvdz; b MP2/6-311++G(2df,2p); c M11/6-311++G(2df,2p)// B3LYP/6-311++G(2df,2p)

The cluster-continuum model at MP2/6-311++G(2df,2p) predicted p*Ka* of 1.89 for hydrazoic acid, which is much closer to experimental value than p*Ka* obtained by CPCM. The p*Ka* for H2N3+ (as) and H2N3+ (s) was found to be -7.85 and -18.15, respectively.

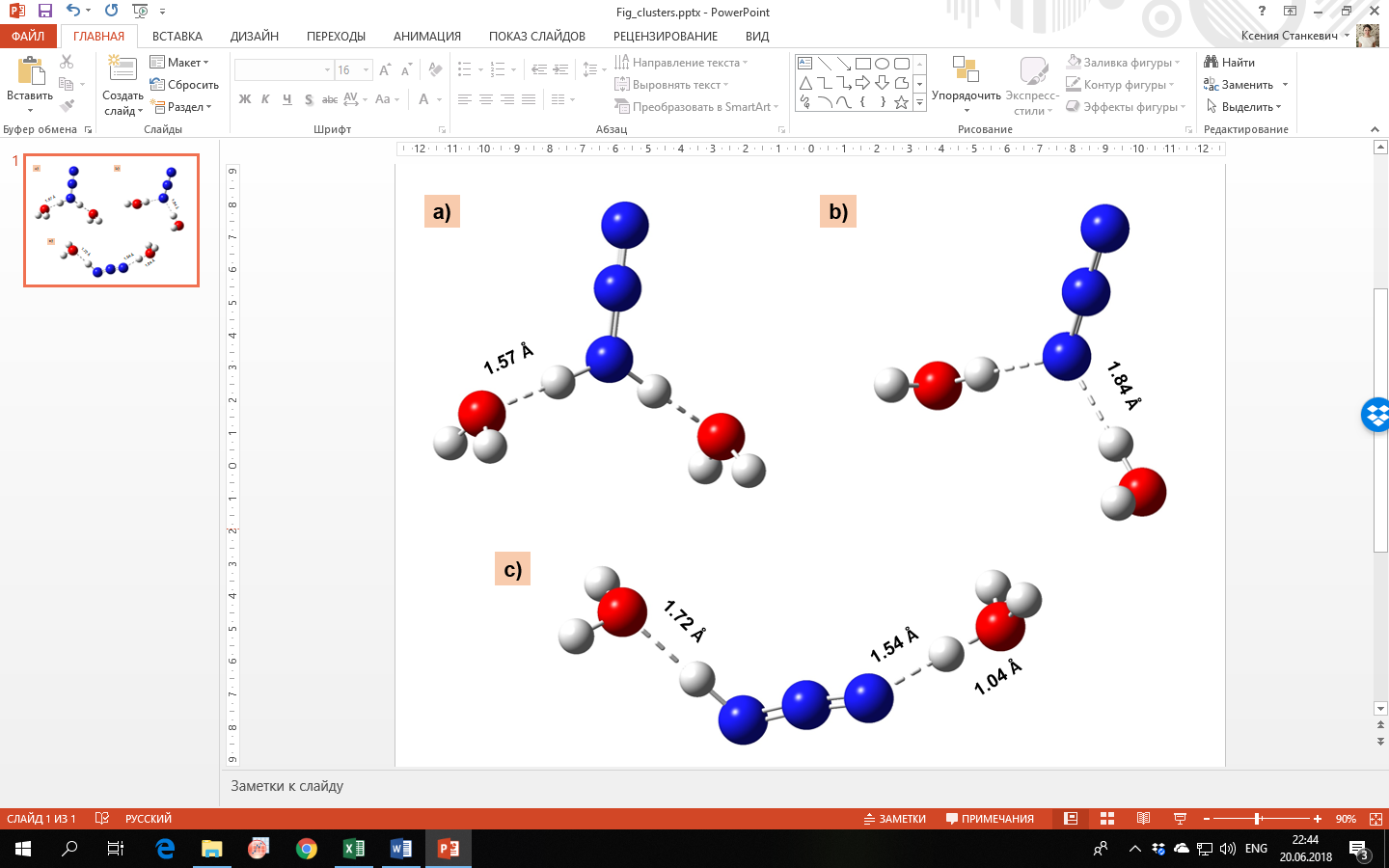


Fig. 2. Optimized geometries for the clusters (B3LYP/6-311++G(2df,2p)): a) H2N3+ (as) (H2O)2; b) N3- (H2O)2; c) H2N3+ (s) (H2O)2.

In order to improve the accuracy p*Ka* calculations we conducted geometry optimization of the obtained clusters using B3LYP functional, which has already shown good results for geometry prediction of the studied species (Table 2). Then, we performed a frequency job with Gaussian09 using range-separated hybrid meta-GGA functional M11 intended for main group thermochemistry 33. The calculated p*Ka* for hydrazoic acid was 4.39, much less deviating from the experimental value than p*Ka* found at MP2/6-311++G(2df,2p) level of theory. The p*Ka* for H2N3+ (as) and H2N3+ (s) was found to be -5.32 and -17.45, respectively.

The geometries of the obtained clusters are shown in Fig. 2. The H2N3+ (as) is strongly solvated: the hydrogen bond distance in H2N3+ (as) (H2O)2 is close to the one in H3O+(H2O)3 (Fig.1S a) and is shorter than in N3- (H2O)2 (Fig.2). The H2N3+ (s) (H2O)2 geometry shows the proton transfer from H2N3+ (s) to H2O (Fig.2).

Thus, the H2N3+ (s) and H2N3+ (as) were predicted to be much stronger acid then HN3. In turn, the H2N3+ (s) was predicted to be a stronger acid than H2N3+ (as). This is in agreement with the fact that H2N3+(as) is more thermodynamically favourable and, therefore, more stable than H2N3+(s). Considering previous studies of H2N3+ structure 18,29, it is unlikely that the H2N3+ (s) can be obtained experimentally or participates in direct amination. Thus, its’ p*Ka* calculation has rather fundamental interest than practical. In contrast, the p*Ka* found for H2N3+ (as) has a great practical importance since it allows us not only to explain the accumulated experimental results, but also to finally clarify the conditions required for direct amination. It was observed that direct amination using N3- does not proceed in trifluoroacetic acid 19 (p*Ka*=0.52 34) and gives poor yields in sulfuric acid (p*Ka*(1)=-2.8; p*Ka*(2)=1.92) 35, whereas sound results were obtained using CF3SO3H (*H0*=-14.1 21) 20, CF3COOH/CF3SO3H 19, BF3-H2O (*H0*=-11.4) 21, AlCl3-HCl 18,34 (*H0*=-0.92 ) and AlCl3-H2SO4 17. Considering predicted p*Ka* for H2N3+ (as) we can conclude that CF3COOH and H2SO4 are stronger than hydrazoic acid but weaker than H2N3+ (as) (Table 3), while in other cases acids are stronger then both hydrazoic acid and H2N3+ (as) (Table 3). Thus, an acid stronger than H2N3+ (as) with p*Ka* lower than approximately -5.32 is required for the direct amination with HN3. As we can see, such an acid can be found among superacids or Lewis acids.

**Mechanism of direct amination**

Herein, we consider two possible pathways **A** and **B** of direct amination (Scheme 1) proposed earlier elsewhere 18–21. Both of them refer to electrophilic aromatic substitution. However, in the first one the H2N3+ (as) acts as electrophile (pathway **A**), while in the second one the H2N3+ (as) decomposes giving NH2+, which then acts as electrophile (pathway **B**) (Scheme 1).

If we assume that direct amination follows the pathway **B** we need to assess the energy required for the electrophile generation.



Scheme 2. Thermodynamic characteristics of NH2+ formation from H2N3+ (as) calculated at B3LYP/aug-cc-pvdz level of theory in (a) gas phase and (b) water (CPCM solvation model).

As can be seen from Scheme 2, the energy of bare NH2+ formation from H2N3+ (as) is 79.8 kcal/mol. This energy difference can be reduced to 46.65 kcal/mol if NH2+ appears in triplet state. However, nitrenium ion in singlet state has a vacant *p* orbital and a lone electron pair, thus, it is more likely that it would act as electrophile. Thus, in pathway **B** the energy required for the generation of electrophile is 79.8 kcal/mol. Solvation decreases the energy of NH2+ formation from H2N3+ (as) from 79.8 kcal/mol to 62.39 kcal/mol. It is important to note that the energy of Nα-Nβ bond cleavage in H2N3+ (as) is significantly higher than the energy of nitrogen elimination from aromatic diazonium cations PhN2+ (eq 10). The latter equals 27 kcal/mol according to experimental data and theoretical calculations [see, for example, 10.1002/chem.200400386].

(10)

Such a high strength of Nα-Nβ bond in H2N3+ (as) is due to a high free energy of NH2+ (singlet) comparing to Ph+. Thus, if we consider only dediazotization energy as a criterion of diazonium cations stability, we can conclude that among aryl- and alkyl-diazonium cations aminodiazonium cation H2N3+ (as) should be the most stable one.

If we consider pathway **A** for direct amination we need to locate the structures and free energies of stationary points on the potential energy surface (PES) of the reaction. Using benzene as an example, we followed the classical electrophilic aromatic substitution mechanism and found the structures and free energies of π-complex, σ-complex and corresponding transition states (Fig.3, Scheme 5).



Fig.3. Structures of the stationary points on the potential energy surface in the direct amination of benzene by H2N3+ (as). The bond distances (angstroms) and bond angles (degrees) are shown according to the results of calculations at B3LYP/aug-cc-pvdz level of theory.

The calculation results predict amination to be thermodynamically favorable. The Gibbs free energy change in the reaction of anilinium ion and nitrogen formation from benzene and H2N3+ (as) is -85.75 kcal/mol (eq 11).

(11)

The data for the substituted arenes are given in Table 5 and will be discussed further. Here we should only note that amination remains thermodynamically favorable for both activated and deactivated substrates.

As can be seen from Fig.3, benzene and H2N3+ (as) form a C atom coordinated π-complex with a C-N distances of 3.07-3.39 Å. The strong interaction and charge transfer between H2N3+(as) and benzene in π-complex facilitate the further decomposition of H2N3+ (as)  observed in TS1 (-523.52 cm-1). The geometry of TS1 shows an increased Nα-Nβ bond length of 1.59 Å in H2N3+ (as) specie and decreased CAr-Nα distance of 2.44 Å indicating that Nα-Nβ bond cleavage in H2N3+ (as) is accompanied by simultaneous formation of C- Nα bond between appearing NH2+ and benzene. In σ-complex the C-Nα distance reduces to 1.41 Å, whereas Nα-Nβ distance increases to 3.39 Å demonstrating the final appearance of C- Nα bond and release of nitrogen. A comparison of the C-N distance in π-complex, TS1, and σ-complex shows that TS1 has a structure more similar to π-complex. Thus, according to the Hammond postulate the direct amination has an earlier transition state than halogenations since halogenations show a closer structural similarity between the σ-complex and corresponding transition state 37–39. Taking into account the structure of the σ-complex it seems likely that the amino group would serve as a base in the deprotonation of the arenium ion. Indeed, the found TS2 structure (-1441.53 cm-1) shows the proton moving half-way towards amino group and increased C-N bond length of 1.47 Å close to one in anilinium ion (1.49 Å). The deprotonation of the arenium ion and release of nitrogen result in formation of the anilinium ion, which structure is shown in Fig.3.

The PES for the direct amination of benzene by H2N3+ (as) in gas phase and in water is shown in Scheme 3. The formation of the π-complex in gas phase is an exergonic process by -3.23 kcal/mol, whereas in aqueous solution it is endergonic by 6.45 kcal/mol. Thus, in water the reactants are better solvated than π-complex. The similar changes in energy were observed for the formation of the π-complex in nitration in 37. The rest of the PES profile is similar for the gas phase and water.

|  |  |
| --- | --- |
| **a)** |  |
| **b)** |  |

Scheme 3. Free energies for the stationary points on the PES in the direct amination of benzene by H2N3+ (as) calculated at B3LYP/aug-cc-pvdz level of theory: a) in gas phase; b) in water (CPCM solvation model).

As we can see in both gas phase and water the rate determining step in benzene amination by H2N3+ (as) is the transition state TS1 between π- and σ-complexes, which formation from π-complex in gas phase requires 14.93 kcal/mol (Scheme 3). In TS1 the energy of the Nα-Nβ bond cleavage in H2N3+ (as) is compensated by the energy of new C-N bond formation between the appearing NH2+ and benzene (Fig.3). The stabilization of NH2+ facilitates the release of nitrogen and reduces the energy required for the H2N3+ (as) decomposition from 79.8 kcal/mol (pathway **B**, Scheme 2) to 11.7 kcal/mol comparing to the energy of H2N3+ (as) decomposition with formation of bare NH2+. As a result, the energy required for electrophile generation in the pathway **B** is significantly higher than the energy of rate determining step in pathway **A**, hence the pathway **B** can be ruled out as less thermodynamically favorable.

It could be noted that TS1 is higher in free energy in aqueous solution than in gas phase, which lead to the conclusion that amination is better proceed in non-polar media rather than in polar. Indeed, Borodkin *et al* demonstrated that in most cases the use of solvents with low polarity results in better yields of the amination product 36.

Thus, for the first time we have clearly shown that the pathway **A** is thermodynamically favored over the pathway **B** and direct amination of arenes by hydrazoic acid proceeds via H2N3+ (as) as electrophile. Also, we demonstrated that direct amination refers to electrophilic substitution reactions, which rate is determined by the transition state TS1, and it better proceeds in non-polar media.

In order to study the influence of the substitution in aromatic ring on the structure and energies of the stationary points on amination PES we took five monosubstituted benzenes: toluene, aniline, anisole, chlorobenzene, and nitrobenzene.

Taking para isomer as an example, we may see that with an increase of ionization potential (PI) of the corresponding substituted benzene the distance between the *para*-carbon (C4) and Nα in π-complex increases. The shorter C4-Nα distance in π-complexes of benzenes with electron-donating substituents indicates stronger interaction and a more significant charge transfer between H2N3+ (as) and a substrate. This further facilitates the formation of TS1 since less structural changes, and as a result, less energy are required (Table 4). It should be also noted that positional selectivity in amination already occurs in π-complexes. For example, *para*-oriented π-complexes give *para*-oriented TS1 (Fig.4). Moreover, the formation of *para*-oriented π-complexes is thermodynamically favoured over *ortho-* and *meta-* (Table 5)*.* The exception is nitrobenzene, where no specific carbon coordination is observed in π-complex.

Table 4. *Para*-carbon and Nα distances in π-complexes (*dπ*), TS1 (*dTS1*) and σ-complexes (*d*σ) and differences in free energies between TS1 and π-complexes (Δ*GTS1-π*) and σ-complexes and TS1 (Δ*G*σ-*TS1*) for *para*-substituted anilines.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| PhX; X= | PI 40, eV | *dπ*, Å | *dTS1*, Å | *d*σ, Å | Δ*dTS1-π*, Å | Δ*GTS1-π*, kcal/mol | Δ*dTS1-*σ, Å | Δ*G*σ-*TS1*, kcal/mol |
| NH2 | 7.7 | - | 2.60 | 1.46 | - | - | 1.136 | -71.88 |
| OMe | 8.22 | 2.89 | 2.53 | 1.46 | 0.353 | 12.18 | 1.083 | -67.60 |
| Me | 8.82 | 2.97 | 2.47 | 1.44 | 0.504 | 13.61 | 1.035 | -61.81 |
| H | 9.245 | 3.07 | 2.44 | 1.41 | 0.626 | 14.93 | 1.030 | -57.79 |
| Cl | 9.07 | 3.17 | 2.47 | 1.44 | 0.699 | 13.93 | 1.033 | -58.84 |
| NO2 | 9.92 | 3.28a | 2.41 | 1.38 | 0.867 | 14.56 | 1.032 | -51.19 |

a In case of nitrobenzene no specific carbon orientation was observed in π-complex

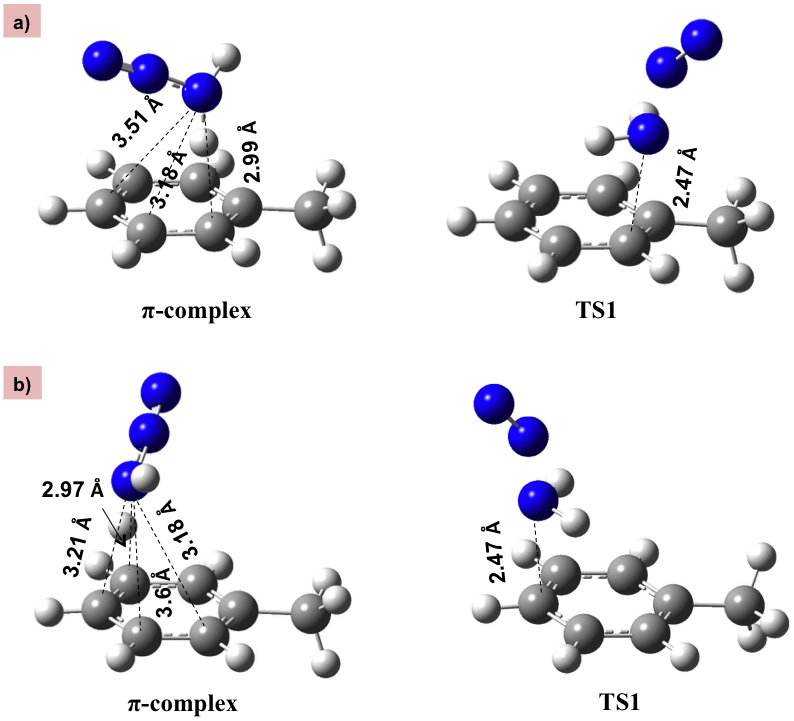


Fig.4. Structures of π-complexes and TS1 for *ortho-* (a) and *para-* (b) aminotoluidines formation (B3LYP/aug-cc-pVDZ).

The opposite relationship is observed between the PI and C4-Nα distance in TS1: with a decrease of PI the C4-Nα distance increases (Table 4). Indeed, the more activating substituent is the earlier rate determining TS1 is observed as the reaction rate increases 37. Therefore, the structures and energies of rate determining TS1 of substrates with electron-donating substituents is further away from the corresponding σ-complexes. The length of the C4-Nα bond in σ-complexes decreases with an increase of PI (Table 4). Obviously, the stronger electron-withdrawing substituent stimulates the more pronounced electron donating effect of amino group, which results in a higher conjugation of appearing amino group and aromatic ring and shorter C4-Nα bond length.

Table 5 shows the free energies of the stationary points on the PES for the direct amination of toluene, aniline, anisole, chlorobenzene and nitrobenzene by H2N3+ (as).

Toluene is activated in SEAr and *ortho-*/*para-* directing. The formation of *ortho-* and *para-* oriented π-complexes between toluene and H2N3+ (as) is thermodynamically favorable with *para-* position preferred over *ortho-*. Unfortunately, we were not able to find *meta-* oriented π-complex since during optimization it converged to *para-*. For toluene the formation of TS1 is a rate determining step with the lowest activation energy for *para-* position. The thermodynamics of σ-complexes and TS2 formation shows that in both cases *para-* isomer is the most favorable and *meta-* isomer is the least favorable. However, according to the experimental results the *para:ortho* ratio is in a range of 0.54-0.81 18–21. It is explained by the statistical factor: in toluene there are two equally activated available *ortho*- positions and only one *para-* position, which leads to an increased *ortho-* content. Among the products the most thermodynamically favorable is *meta-* toluidinium ion and the least thermodynamically favorable is *ortho-* toluidinium ion. The *ortho*- isomer rearrangement to *meta-* could explain an increased *meta-* and decreased *ortho-* content observed in some papers 15,16.

Anisole is activated in SEAr and *ortho-*/*para-* directing. The formation of *para-* oriented π-complex between anisole and H2N3+ (as) requires -7.21 kcal/mol and is more thermodynamically favourable then for toluene. Unfortunately, we were not able to locate *ortho-* and *meta-* oriented π-complexes. The energy required for TS1 formation for anisole is also reduced comparing to benzene and toluene with *para-* position preferred over *ortho-*. The same is observed in σ-complexes, whereas in TS2 and products *ortho-* isomer is thermodynamically favoured over *para-* (Table 5). We have not shown data for *meta-* oriented σ-complex and TS2 since a proton transfer with the formation of arenium ion was observed in both cases (Fig.2S a). Overall, the calculations are in agreement with experimental data, where *para:ortho* ratio for anisole lies in a range of 1.21 to 1.86 18–19, 21.

Chlorobenzene is deactivated in SEAr, but *ortho-*/*para-* directing. The formation of π-complex between chlorobenzene and H2N3+ (as) is less thermodynamically favourable then for benzene and toluene. Same as for toluene, for chlorobenzene the TS1 is a rate determining step with the lowest activation energy for *para-* position. In σ-complexes and TS2 of the chlorobenzene *para-* isomer is also the most thermodynamically favorable and *meta-* isomer is the least thermodynamically favorable. The calculations are in agreement with experimental data, where *para:ortho* ratio for chlorobenzene varies from 1.29 to 1.97 18–19, 21.

Nitrobenzene is strongly deactivated in SEAr and *meta-* directing. The π-complex formation between nitrobenzene and H2N3+ (as) requires 7.82 kcal/mol and show no positional selectivity. Unfortunately, we were not able to find TS1 for *meta-* isomer, but σ-complexes energies indicate *meta-* position as the most thermodynamically favorable one (Table 5). Indeed, the amination of nitrobenzene resulted in trace amount of *meta-* isomer 16. The TS2 and products thermodynamics predicts *ortho-* position favored over *meta-*, however, considering TS1 energies it is unlikely that *ortho-* or *para-* isomers can be formed.

Aniline is the most activated and *ortho-*/*para-* directing. For aniline we have found only *ortho-* oriented π-complex. *Meta-* oriented π-complex during optimization converged to *para-*. In *para-* oriented π-complex a proton transfer with the formation of arenium ion was observed (Fig.2S b). The calculations show that the formation of found π-complex should proceed easily and is followed by TS1 with the lowest activation energies among the studied compounds. The *para-* position is thermodynamically favoured in TS1, TS2 and products, whereas in σ-complexes the *ortho*- isomer is preferable (Table 5). Thus, the amination of aniline is thermodynamically possible; however, it has not been reported. In specially conducted experiments we aminated aniline using NaN3 in CF3SO3H. We were able to obtain only traces of phenylene diamine after continuous heating of aniline with an excess of NaN3 in CF3SO3H. It could be caused by the following reasons. First, aniline is obviously a stronger base then H2N3+ (as), thus it would replace it from its salt leading to a decrease in electrophile concentration. It would explain why an excess of reagent is needed to obtain at least traces of the product. Second, in the strong acidic media there is equilibrium between aniline and anilinium ion. The latter is deactivated in SEAr reactions due to electron-withdrawing effect of NH3+. For better understanding of aniline sluggishness in direct amination, we aminated 1-aminenaphtalene in the same conditions as for aniline and obtained 1,5-diaminonaphtalene as a major product with 30% yield. The fact that amination mostly took place in the 5 position indicates that the assumption about electron-withdrawing effect of NH3+ is reasonable.

Table 5. Free energies difference from reactants for the direct amination of aniline, anisole, toluene, benzene, chlorobenzene and nitrobenzene by H2N3+ (as).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **PhX; X=** | NH2 position | ΔG difference from reactants, kcal/mol | | | | |
| **π-complex** | **TS1** | **σ-complex** | **TS2** | **Products** |
| **NH2** | *ortho-* | -9.38 | 2.60 | -73.90 | -35.54 | -90.45 |
| *meta-* | -a | - a | -b | -41.12 | -91.53 |
| *para-* | - b | -0.13 | -72.01 | -41.55 | -91.75 |
| **OMe** | *ortho-* | -b | 6.20 | -61.37 | -91.97 | -36.80 |
| *meta-* | - a | - a | -b | -b | -35.77 |
| *para-* | -7.21 | 4.98 | -62.63 | -83.06 | -36.16 |
| **Me** | *ortho-* | -4.34 | 9.42 | -51.96 | -31.15 | -86.71 |
| *meta-* | - a | **9.65** | -49.21 | -30.70 | -87.59 |
| *para-* | -5.25 | 8.36 | -53.46 | -32.47 | -86.78 |
| **H** | ***-*** | **-3.23** | **11.70** | **-33.24** | **-28.01** | **-85.75** |
| **Cl** | *ortho-* | -c | 14.04 | -43.73 | -24.55 | -83.31 |
| *meta-* | 0.65 | - a | -40.41 | -22.78 | -80.92 |
| *para-* | -0.31 | 13.63 | -45.21 | -25.00 | -81.21 |
| **NO2** | *ortho-* | 7.82 | 18.03 | -28.66 | -14.82 | -80.91 |
| *meta-* | -d | -31.25 | -14.52 | -74.92 |
| *para-* | 22.39 | -28.80 | -14.27 | -74.33 |

a During optimization *meta-* position converged to *para-*

b Proton transfer was observed

c We were not able to find a π-complex

d We were not able to find TS1

**Direct amination among** **the *SEAr* reactions**

In attempt to find out the place of direct amination among the other *SEAr* reactions we calculated the rate constants for the amination of studied compounds using Eyring–Polanyi equation (eq 12) considering the energy of TS1 formation as ΔG≠ and then found the relative ksubstrate/kbenzene rate:

(12)

where *ΔG≠* is the Gibbs energy of activation, *κ* is the transmission coefficient (κ=1), *kB* is Boltzmann's constant, *h* is Planck's constant, *R* is gas constant, and *T* is absolute temperature (T=298.15 K).

We calculated the theoretical reaction constant *ρ* by plotting lg ksubstrate/kbenzene for *para-* position over the σ+ values of corresponding substituents 41 (-NH2, -OMe, -Me, -H, -Cl, -NO2). The plot showed a good correlation between lg ksubstrate/kbenzene and σ+ with *R2* of 0.989 and a *ρ* value of -8.5, which allowed us to put amination of arenes by HN3 somewhere in-between nitration and halogenations. As we stated above, amination is characterized by an earlier transition state than halogenations since TS1 in amination shows more similarity to the π-complex, whereas TS in halogenations is more similar to the σ-complex 38,39. Thus, it is reasonable that *ρ* calculated for amination is higher (Table 6) than observed for halogenations.

Table 6. The reaction constants for *SEAr* reactions

|  |  |
| --- | --- |
| **Reaction** | ***ρ*** |
| Bromination (CH3COOH) 41 | -13.1 |
| Chlorination (CH3COOH+H2O) 41 | -13.0 |
| Acylation (CH3COCl, AlCl3, C2H2Cl2) 41 | -8.6 |
| ***Amination (HN3)*** | ***-8.5*** |
| Nitration (H2SO4+HNO3) 41 | -6.4 |
| Amination (PhXN3, AlCl3) 42 | -6.0 |
| Amination (PhXN3, CF3COOH, CF3SO3H) 43 | -4.5 |

Nitration was also shown to have an earlier transition state than halogenations 37. It is quite complicated to compare nitration and amination in terms of TS location. On the other hand, it is well known that nitration of aniline gives a mixture of *para-* and *meta-* isomers in a ratio of 51% to 47% with 95% yield, while amination of aniline results in only traces of product. In both cases aniline forms a conjugated acid due to strong acidic conditions and becomes deactivated. However, it still undergoes nitration in rigorous conditions, while more sluggish to amination. We may observe the same situation for nitration and amination of nitrobenzene. From this point we may say that amination is quite similar to a Friedel-Crafts alkylation and acylation, which also do not proceed with strongly deactivated substrates. ~~On the other hand, the fact that H~~~~2~~~~N~~~~3~~~~+~~~~(as)~~ ~~is still able to substitute both activated and deactivated substrates (e.g. chlorobenzene~~ ~~18–19, 21~~~~, fluorobenzene~~ ~~19~~~~) allows us to put H~~~~2~~~~N~~~~3~~~~+~~~~(as)~~ ~~in one row with such electrophiles as NO~~~~2~~~~+~~~~, Br~~~~2~~~~-MX~~~~n~~~~, Cl~~~~2~~~~-MX~~~~n~~~~, etc.~~

Thus, direct amination refers to electrophilic substitution reactions with an early transition state ~~and overall can proceed with both activated and deactivated substrates, which allows us to put H~~~~2~~~~N~~~~3~~~~+~~~~(as)~~ ~~in one row with such electrophiles as NO~~~~2~~~~+~~~~, Br~~~~2~~~~-MX~~~~n~~~~, Cl~~~~2~~~~-MX~~~~n~~~~, etc.~~

**Future of direct amination**

Strong acidic conditions required for amination of arenes with HN3 significantly reduce the number of substrates suitable for amination. To overcome this problem, the derivatives of H2N3+ (as) can be used, for example, phenylaminodiazonium ion (PhHN3+). For comparison, we found the thermodynamic characteristics of PhNH+ formation from PhHN3+ (Scheme 4).



Scheme 4. Thermodynamic characteristics of PhNH+ formation from PhHN3+ in gas phase.

The conjugation between of NH+ and aromatic ring stabilizes the appearing nitrenium ion and significantly decreases energy of nitrogen cleavage making the process of PhNH+ formation thermodynamically favourable. The calculation results are supported by the fact that arylazides react with benzene giving diphenylamines in the presence of CF3COOH 43. However, the mechanism of direct amination of arenes by PhHN3+ and its derivatives require special investigation.

Apparently, the use of organic azides for amination might be promising as reaction would proceed in milder conditions.

**Conclusions**

Overall, for the first time using DFT we have shown that direct amination of arenes by hydrazoic acid follows the classical *SEAr* mechanism with aminodiazonium cation H2N3+ (as) as electrophile. The located stationary points allowed us to define direct amination as *SEAr* reaction, which rate is determined by the transition state between π- and σ-complexes. The positional selectivity in amination already occurs in π-complexes making their formation an important step along the reaction pathway. The structural similarity between the transition state and π-complex shows that direct amination has an early transition state. The comparison of amination and other *SEAr* reactions in terms of transition state location using the reaction constant *ρ* allowed us to place it somewhere in-between nitration and halogenations closer to nitration. ~~Taking into account the fact that amination proceeds with both activated and deactivated substrates we may put H~~~~2~~~~N~~~~3~~~~+~~~~(as)~~ ~~in one row with such electrophiles as NO~~~~2~~~~+~~~~, Br~~~~2~~~~-MX~~~~n~~~~, Cl~~~~2~~~~-MX~~~~n~~~~, etc~~. We also showed that amination by HN3 better proceeds in non-polar media rather than in polar. For the first time we have studied the acidity of hydrazoic acid and H2N3+ and calculated their p*Ka*. We have shown that an acid stronger than H2N3+ (as) with p*Ka* lower than approximately -5.32 is required for the direct amination with HN3, which explains why amination took place only in the presence of superacids or Lewis acids. These results open a prospect for identification of the new aminating agents working in milder conditions.

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**Experimental section**

**General**

All the reagents were ACS grade and used without further purification. 1Н NMR and 13С NMR spectra were recorded using Bruker AVANCE III HD spectrometer at 400 MHz and 100.5 MHz, respectively. IR spectra were recorded in ATR mode (ZnSe crystal) with Agilent Cary 630 FTIR (Agilent Technologies, USA). GC/MS analysis was performed using Agilent 7890/5975C system. Melting points (uncorrected) were measured using melting point system MP50 (Mettler, Toledo).

**Synthesis of benzene diamine**

Sodium azide (8 mmol, 520 mg) was added by four piecemeal every hour to a solution of aniline (2 mmol, 0,182 ml) in triflic acid (2 ml). The reaction mixture was heated at 60 оС for two weeks with stirring. The progress of the reaction was monitored by the consumption of the starting aniline using TLC (eluent – ethylacetate/hexane=2/1). The analysis of the reaction mixture by GS and GC/MS showed two compounds: aniline and benzene diamine.

**Aniline:** GC-MS (EI), T retention 4.963 min: m/z (%) = 93 (100) [M+], 92 (12.5), 66 (32.5), 63 (5), 52 (4.5).

**Benzene diamine:** GC-MS (EI), T retention 8.838 min: m/z (%) = 108 (100) [M+], 107 (14.5), 91 (4.5), 80 (45.5), 53 (13.5).

**Synthesis of naphthalene-1,5-diamine**

Sodium azide (8 mmol, 520 mg) was added by four piecemeal every hour to a solution of naphthalen-1-amine (2 mmol, 286 mg) in triflic acid (2 ml). The reaction mixture was heated at 60 оС for two weeks with stirring. The progress of the reaction was monitored by the consumption of the starting naphthalen-1-amine using TLC (eluent - ethylacetate/hexane=2/1). The reaction mixture was poured into water (50 ml), neutralized by NaOH until pH 7-8 and extracted with ethylacetate. Organic layer was dried over Na2SO4 and the solvent was removed under reduced pressure. Total yield was 0.3542 mg (100%). Purification by column chromatography using ethylacetate over silica gel gave two major fractions: first fraction (1-aminonaphtalene), yield 0.2173 mg (61%), second fraction (1,5-diaminonaphtalene**)**, yield 0.1058 mg (30%).

**1-aminonaphtalene:** Pink solid; yield 0.2173 mg (61%). m.p. 50-51 оС (lit. m.p. 48-50 оС 23). 1H NMR (400 MHz, DMSO-*d6*): δ = 8.07 (*d*, J= 8 Hz, 1H, 8-CHAr), 7.73(*d*, J= 8 Hz, 1H, 5-CHAr), 7.38 (*m*, 2H, 6,7-CHAr), 7.21 (*m*, 1H, 3-CHAr), 7.08 (*d*, J= 8 Hz, 1H, 4-CHAr), 6.69 (*d*, J= 8 Hz, 1H, 2-CHAr), 5.72 (*s*, NH2) ppm. 13C NMR (100.5 MHz, DMSO-*d6*): δ = 145.15, 134.65, 128.28, 127.21, 125.95, 124.10, 123.10, 122.80, 115.85, 107.90 ppm. IR: 3411 cm-1, 3340 cm-1, 3230 cm-1. GC-MS (EI), T retention 11.061 min: m/z (%) = 143 (100) [M+], 116 (18), 115 (43), 89 (5), 71.5 (7), 63 (5).

**1,5-diaminonaphtalene:** Brown solid; yield 0.1058 mg (30%). m.p. 187 оС (lit. m.p. 188 оС 44). 1H NMR (400 MHz, DMSO-*d6*): δ = 7.22(*d*, J= 8 Hz, 2H, 4,8-CHAr), 7.07 (*m*, 2H, 3,7-CHAr), 6.61 (*d*, J= 8 Hz, 2H, 2,6-CHAr), 5.44 (*s*, NH2) ppm. 13C NMR (100.5 MHz, DMSO-*d6*): δ = 144.97, 124.82, 124.22, 110.47, 107.90 ppm. IR: 3424 cm-1, 3413 cm-1, 3320 cm-1, 3226 cm-1. GC-MS (EI), T retention 13.757 min: m/z (%) = 158 (100) [M+], 141 (4), 131 (6), 130 (27), 118 (5), 103 (9), 79 (9), 65 (4).

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