

# Density functional study of *ortho*-substituted phenyl cations in polar medium and in the gas phase

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## ABSTRACT

Density functional theory (DFT) calculations of several 2-X-substituted phenyl cations (X = 2-CHO, 2-CH<sub>2</sub>OH, 2-CH<sub>3</sub>, 2-CH=NH, 2-OCH=NH, 2-SCH=NH, 2-CH=CH-CH=CH<sub>2</sub>, 2-CH=CH<sub>2</sub> and 2-NO<sub>2</sub>) have been carried out in the gas phase and in acetonitrile (MeCN) at the B3LYP/6-31G(d,p) level of theory. The stationary point geometry of these aryl cations have been found to be in strong dependency of the medium. In the gas phase, unexpected behavior of considered aryl cations takes place resulting in the rearrangement or ring closure reaction. Such the cyclization reaction is proceeding *via* the nearby atom of the substituent which appears in relative vicinity (up to ~3 Å) to the cationic center. Only in the case of 2-NO<sub>2</sub> derivative, the geometry optimization has lead to rearranged quazi-quinoid structure of the cation that, obviously, takes place because of instability of the ring formed. Scan of the potential energy surface (PES) of 2-nitrophenyl cation has displayed no any reaction path leading toward the rearranged structure. Thus, the impossibility of existing of the singlet state of 2-nitrophenyl cation in the gas phase has been offered. The singlet-triplet transition of 2-nitrophenyl cation has been discussed in terms of the spin-orbit coupling (SOC) effects.

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## 1. Introduction

Lately, the aryl cations became a subject of the attractive studies for few groups of scientists [1–5]. Since the postulation of the phenyl cation as a reaction intermediate [6], a number of reports studying reactivity and stability of the aryl cations have been published [7–10]. One of the most efficient methods for the aryl cations generation is dediazotization of diazonium salts which is usually conducted in polar solvents [11,12]. Another type of reaction yielding the aryl cations is photoheterolysis of haloanilines [13] as well as the gas phase decay of multitritiated hydrocarbons [9,14]. The aryl cations formed this way are expected to be at the triplet states [15], but it is only in the case of *para*-substituted cations with electron donating groups in the benzene nucleus [4,5].

Especially interesting features of the aryl cations are relatively small singlet-triplet energy gap and the nature of the ground state multiplicity. It was found earlier [4,5,7,8] that phenyl cation has ground singlet (<sup>1</sup>A<sub>1</sub>) state, while the first triplet (<sup>3</sup>B<sub>1</sub>) state has excitation energy being equal to 75–100 kJ mol<sup>−1</sup>. These theoretical results were proved by Winkler and Sander [16,17] by isolation of the phenyl cation in a solid argon matrix and IR spectroscopic study. The ground state multiplicity of *para*-substituted aryl cat-

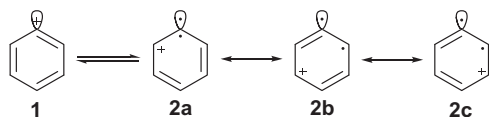
ions was found to be the triplet, when X = NH<sub>2</sub>, N(CH<sub>3</sub>)<sub>2</sub>, OH, OCH<sub>3</sub>. It also should be note that these computational results are almost independent of the basis set chosen, as it can be seen from Refs. [4,5].

Meanwhile, the aryl cations containing electron withdrawing groups in the benzene ring were postulated to have the singlet ground state multiplicity. And to the best of our knowledge, we did not find any data regarding the theoretical or experimental study of such the cations as well as extended study of the cations with substituents in the *ortho*-position, except one [18]. As the aryl cations are widely appeared during both the gas and liquid phase reactions it would be useful to compare the reactivity and stability of these species in different conditions. The behavior of *ortho*-substituted aryl cations with strong electron withdrawing groups is especially interesting, since these are usually containing electron rich atoms (*viz.* O, N, S, etc.). The tandem of electron rich atom with strong electrophilic center (an empty  $\sigma$ -orbital of the carbon ring) lying in relative affinity to one another is promising to display quite unusual results.

The above parent phenyl cation has the ground singlet <sup>1</sup>A<sub>1</sub> state, while the lowest excited triplet state is <sup>3</sup>B<sub>1</sub>. These two states lie on different PESs, thus the interconversion between them is non-adiabatic spin-forbidden process [19]. Indeed, the singlet-triplet excitation proceeds due to the SOC effect between two interacting PESs in the vicinity of areas where they cross forming one of the following structures.

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Structure **2a** here provides the largest contribution to the total wave function, as follows from our analysis of the spin density [20]. The  $S \rightarrow T$  transition (**1**  $\rightarrow$  **2a**) is effectively allowed, according to classification of spin-forbidden reactions [21], since it includes one-center SOC integral. This point is characterized by energetically identical levels for both the singlet and triplet states. To estimate the speed of this process, it is necessary to determine the minimum energy crossing point (MECP) where two surfaces cross, and the coupling constant between them at this point [22].

In this study, we predict and analyze the possibility of absolutely new type of ring closure reactions, which are preliminary prompted and particularly showed by few previous experimental facts [23–26].

## 2. Computational details

Calculations have been performed using the Gaussian03 program suite [27]. Geometry optimizations have been carried out using DFT [28] method at the B3LYP [29,30] /6-31G(d,p) [31] level of theory. Vibrational frequencies at the B3LYP/6-31G(d,p) level have been used to characterize stationary points as minima (number of imaginary frequency (NIMAG)=0) and to evaluate zero-point vibrational energies (ZPVE), which have been scaled by a factor of 0.98. Total energy has been defined as the internal energy at 0 K for calculated aryl cations as follows:

$$U_0 = E_{\text{elec}} + \text{ZPVE},$$

where  $E_{\text{elec}}$  is the energy for the stationary point on the Born–Oppenheimer PES. As the starting geometry for calculations of the aryl cations, the corresponding N≡N group detached aryl diazonium cations have been utilized. Their geometries have also been optimized and their IR frequencies have been found to be real.

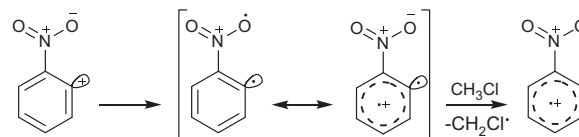
The simulation of the medium has been performed by employing of the polarized continuum model (PCM) [32] with set value of dielectric permittivity being equal to 36.64 that corresponds to acetonitrile. Calculations of the triplet aryl cations have been performed with the spin-unrestricted Kohn–Sham formalism. Electronic spectra of 1-chloro-2-nitrobenzene have been calculated using the time dependent density functional theory TD DFT [33–35]. The transition states for the ring closure reaction have been found using the synchronous transit-guided quasi-Newton method [36,37]. The intrinsic reaction coordinate (IRC) calculations have been performed using Fukui theoretical background [38].

## 3. Results and discussion

### 3.1. Optimized geometry of the aryl cations

Primary aim of this extended study has been arisen from unusual results of Filippi et al., which are related to the gas phase chemistry of several *ortho*-substituted aryl cations [18]. A great tribute has been paid there to the behavior of *ortho*-nitrophenyl cation reacting with methyl alcohol (gas, liquid) and chloromethane (gas). The results regarding *ortho*-nitrophenyl cation chemistry in the above study can be itemized as follows: in the liquid phase 2-nitroanisole is formed efficiently, whereas the gas phase reactions with both  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{Cl}$  are completely failed [18]. No any supposed products were obtained in these cases. Among few

proposed hypotheses which account for all the experimental evidences a more plausible rationale involved intramolecular electron transfer from a  $\text{NO}_2$  lone pair to the formally vacant orbital of  $o\text{-O}_2\text{NC}_6\text{H}_4^+$ . The formation of nitrobenzene radical cation is the key step of the proposal.



All the mentioned suppositions are based on the DFT/RHF/6-31G(d) calculations of 2-nitrophenyl cation. Indeed, the Hartree–Fock method gives the optimized structure of the latter in a form of the aryl cation as also display our repeated calculations. Meanwhile, the utilization of the B3LYP approach, which is well-known as one of the best methods for geometry optimization, is providing a rearranged structure regardless the basis set used or polarization/diffusion functions added. It is not hard to see that such rearrangement is caused by the appropriate position of atoms and orbitals in the cation. Thus, one can suppose that this particular case can be extended for a number of cations with such substituents as 2-CHO (**1**), 2- $\text{CH}_2\text{OH}$  (**2**), 2-CHS (**3**), 2- $\text{CH}=\text{NH}$  (**4**), 2- $\text{OCH}=\text{NH}$  (**5**), 2- $\text{SCH}=\text{NH}$  (**6**), 2- $\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$  (**7**), 2- $\text{NO}_2$  (**8**) and 2- $\text{CH}=\text{CH}_2$  (**9**). The optimized structures of the cations 1–9 are illustrated in the Fig. 1 and the calculated data are listed in Table 1.

Since the discussed rearranged cations are only the reactive intermediates in chemical reactions they need to be stabilized in any way. The most appropriate stabilization path is the deprotonation reaction which was previously shown for the cases of 2-propylbenzene-1-ylum [23,24], 2-isobutylbenzene-1-ylum and 2-neopentylbenzene-1-ylum [24] and 2-butylbenzene-1-ylum [25] yielding indane, 2-methylindane, 2,2-dimethylindane and tetralin, respectively.

The route of deprotonation reaction in the case of the cations **2** and **4–7** is determined by the value of atomic charges on the H-atoms. In 1,2-dihydrobenzo[*b*]oxetium the H-atom which bonded with the oxygen has much higher atomic charge than nearby H-atoms (0.402 vs. 0.216 and 0.233). Thus, the O–H bond is unstable enough and easily cleaves resulting in subsequent 2H-benzo[*b*]oxete formation. It is not hard to predict that in the case of the cations **4–6** the atomic charges on hydrogen atoms will be higher for the H-atoms bonded with the nitrogen rather than carbon (0.328 vs. 0.237 in benzo[*b*]azetium, 0.343 vs. 0.243 in benzo[*d*]oxazol-3-ium and 0.335 vs. 0.243 in benzo[*d*]thiazol-3-ium). Thus, the deprotonation of the cationic precursors **4–6** will lead toward the formation of benzo[*b*]azete, benzo[*d*]oxazole and benzo[*d*]thiazole, respectively. In the case of 1,4-dihydronaphthalen-1-ylum (**7**) there is only one route for the deprotonation leading to naphthalene molecule.

### 3.2. Ring closure reaction mechanism

A simple ring closure reaction is characteristic for the cations **1–7** in the gas phase. At the same time, the geometry optimization in liquid (MeCN) phase provides structures of the species in forms of the aryl cations (**1**, **2** and **4**), whereas for the other species the above reaction occurs efficiently (**3**, **5–7**).

#### 3.2.1. Four-membered ring formation

In this subsection we consider the behavior of 2-formylphenyl, 2-thioformylphenyl, 2-(iminomethyl)phenyl, 2-(hydroxymethyl)phenyl and vinylphenyl cations. These have been chosen because

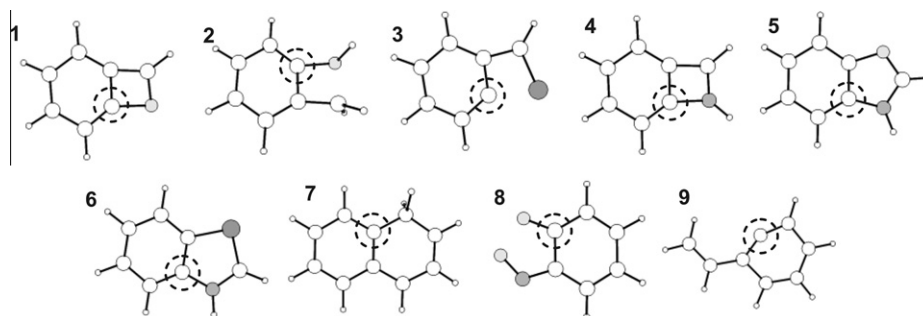


Fig. 1. Stationary geometry of the *ortho*-substituted phenyl cations optimized by the DFT/B3LYP/6-31G(d,p) approach (dashed circles mark the *ipso*-carbon atoms).

**Table 1**  
Singlet–triplet energy gaps, free energy of solvation in MeCN (kcal/mol) and DFT parameters in electronvolts (eV) for the singlet states of a series of cations analyzed in this study.

Entry	Cation	Point group		$\Delta E_{S \rightarrow T}$	$\mu^a$	$\eta^b$	$\omega^c$	$\Delta G_{\text{Solv}}$
		(S)	(T)					
1	2 <i>H</i> -benzo[ <i>b</i> ]oxet-2-ylum	C <sub>s</sub>	C <sub>s</sub>	25.92	−10.57	3.32	16.84	−42.43
2	1,2-dihydrobenzo[ <i>b</i> ]oxetium	C <sub>1</sub>	C <sub>s</sub>	−0.72	−8.61	6.02	6.15	−30.81
3	2 <i>H</i> -benzo[ <i>b</i> ]thiet-2-ylum	C <sub>s</sub>	C <sub>s</sub>	19.99	−10.2	2.75	18.91	−52.59
4	benzo[ <i>b</i> ]azetium	C <sub>s</sub>	C <sub>s</sub>	21.69	−9.68	3.17	14.79	−22.78
5	benzo[ <i>d</i> ]oxazol-3-ium	C <sub>s</sub>	C <sub>1</sub>	68.55	−9.08	5.03	8.18	−59.95
6	benzo[ <i>d</i> ]thiazol-3-ium	C <sub>s</sub>	C <sub>1</sub>	67.67	−8.99	4.58	8.83	−58.11
7	1,4-dihydronaphthalen-1-ylum	C <sub>s</sub>	C <sub>s</sub>	47.94	−9.68	3.53	13.29	−49.31
8	2-vinylbenzene-1-ylum <sup>d</sup>	C <sub>s</sub>	C <sub>s</sub>	0.91	−10.27	2.54	20.8	−52.61
9	2-nitrobenzene-1-ylum <sup>d</sup>	C <sub>s</sub>	C <sub>s</sub>	−2.15	−10.87	3.55	16.62	1.66

<sup>a</sup> Chemical Potential, eV.

<sup>b</sup> Hardness, eV.

<sup>c</sup> Electrophilicity Index, eV.

<sup>d</sup> Name is given for the structure in a form of the aryl cation.

of the different nature of the terminal atom of the substituent (O, S, N and C). Comparison of the behavior of 2-formylphenyl and 2-(hydroxymethyl)phenyl cations, which differ significantly in hybridization of the oxygen and nearby carbon atoms (sp<sup>2</sup> vs. sp<sup>3</sup>), it is necessary. Since the ring closure reaction occurs due to the interaction of formally vacant  $\sigma$ -orbital of the ring carbon atom and the lone pair of the marginal atom of the substituent, it is interesting to evaluate the reactivity of the atoms with different electronegativity.

**3.2.1.1. 2-Formylphenyl cation.** First, we have tried to obtain the transition state (**TS1**), which connects 2*H*-benzo[*b*]oxet-2-ylum and its arylum precursor appearing when N<sub>2</sub> molecule is detached from the corresponding diazonium cation. The obtained **TS1** remains to be planar (symmetry C<sub>s</sub>) with the C<sub>ring</sub>–O interatomic distance being equal to 2.52 Å. In order to confirm that the ring closure reaction is really proceeding *via* the **TS1**, the IRC calcula-

tions have been performed. Fig. 2 displays the energy profile and the geometry transformation along the IRC.

When the reaction proceeds forward from  $s = 0.00$  ( $s$  in amu<sup>1/2</sup> Bohr is the distance from the TS, showing how a geometry along the IRC is different from the TS geometry) to  $s = 5.79$ , the C<sub>ring</sub>–O interatomic distance slightly diminishes. At  $s = 5.79$  amu<sup>1/2</sup> Bohr the C<sub>ring</sub>–O bond appears because of being 1.59 Å in length. Formation of 2*H*-benzo[*b*]oxet-2-ylum is almost complete at this point on the IRC. When the reaction proceeds backward from  $s = 0.00$  to  $s = -4.16$  amu<sup>1/2</sup> Bohr, the TS geometry changes gradually toward 2-formylbenzene-1-ylum structure. The latter cation is too unstable to exist in the gas phase and it must be rearranged immediately after the formation. In order to evaluate the activation energy ( $E_a$ ) of the discussed reaction, we have calculated the 2-formylbenzene-1-ylum with inverted –CHO group. This structure has been found to be stable in the gas phase. Meanwhile, the geometry of the state at  $s = -4.16$  amu<sup>1/2</sup> Bohr on the IRC (Fig. 2) is only

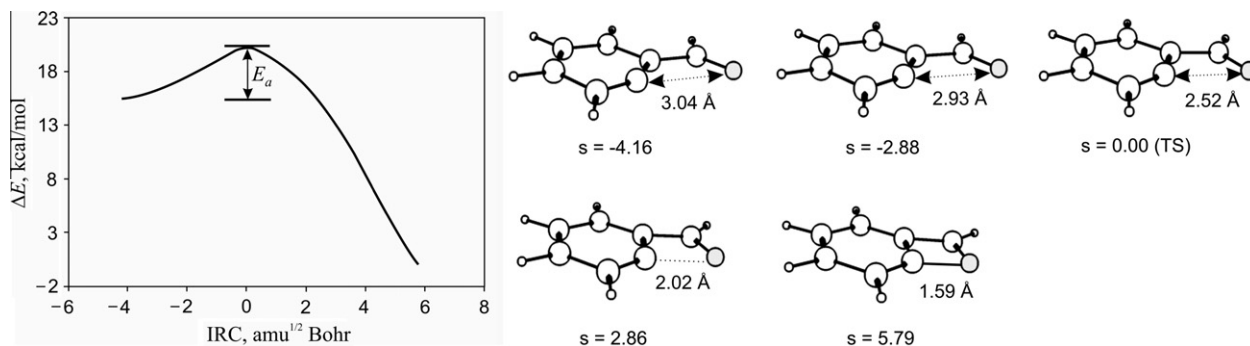
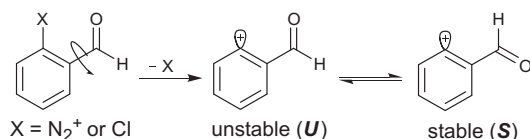


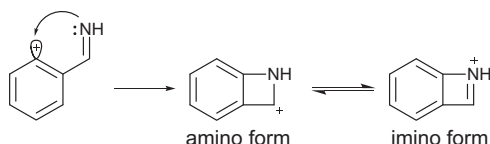
Fig. 2. Potential energy profile and the geometry transformation along the IRC from formally existing 2-formylbenzene-1-ylum to 2*H*-benzo[*b*]oxet-2-ylum.

1.76 kcal/mol higher in energy than the latter suggesting the efficient interconversion.



Thus, the total energy of **S** 2-formylbenzene-1-ylum can be comparable with that of formally existing **U** 2-formylbenzene-1-ylum. The activation barrier  $E_a$ , calculated in this way, has been found to be 6.6 kcal/mol (Fig. 2). The similar reaction pattern is peculiar for the rest of cations included in this subsection. It should be noted that 2-vinylbenzene-1-ylum does not rearrange in both the gas phase and in acetonitrile medium. This is probably because of a smaller nucleophilicity of the marginal side chain carbon atom of the vinyl group, comparatively with the same value for the oxygen, nitrogen or even sulfur atom.

**3.2.1.2. 2-(Iminomethyl)phenyl cation.** The ring closure reaction of 2-(iminomethyl)phenyl cation leads to the formation of benzo[*b*]azetium. The formed product can exist in two forms due to the amino-imino tautomerism (see the scheme below). But the analysis of charge distribution in optimized benzo[*b*]azetium indicates that the nitrogen atom is charged negatively (−0.554), vs. the nearby carbon atom of the four-membered ring (0.308). Thus, the predominant form of benzo[*b*]azetium is the amino form.



Like the previous case, we have calculated the transition state (**TS2**) having the  $C_s$  symmetry and the  $C_{ring}-N$  interatomic distance being equal to 2.80 Å. Scan of the PES (Fig. 3) displays that the **TS2** lies very closely to the starting aryl precursor. As the reaction coordinate became equal to −1.54 amu<sup>1/2</sup> Bohr, the optimization has been stopped favoring the stationary point. In contrast, when the reaction proceeds forward, the optimized product appears at the  $s = 7.27$  amu<sup>1/2</sup> Bohr. It should be noted that this is almost barrierless process with tiny activation energy. The estimated value has

been found to be only 0.32 kcal/mol. Thus, immediately after the formation of 2-(iminomethyl)phenyl cation, it easily overcomes the energetic barrier and gradually shifts to the product.

### 3.2.2. Five-membered ring formation

2-(Iminomethylthio)phenyl and 2-(iminomethoxy)phenyl cations have been chosen in order to extend this study on the five-membered ring formation. These two aryl cations show very similar reaction pattern, therefore we display the potential energy profile only for the case of 2-(iminomethylthio)phenyl cation (Fig. 4). As it can be seen in Fig. 4, the obtained transition state **TS3** is nonplanar with torsion angle  $\tau[C(1)-C(2)-S(3)-C(4)]$  being equal to 95.4°. As the reaction proceeds forward, the  $\tau$  slightly diminishes and the molecule becomes more planar. At the reaction coordinate  $s = 21.58$  amu<sup>1/2</sup> Bohr the formation of benzo[*d*]thiazol-3-ium is complete. On the other hand, the stationary point occurs just almost at start ( $s = -1.48$  amu<sup>1/2</sup> Bohr) when one follow the reaction path in reverse direction. This point corresponds to the geometry of 2-(iminomethylthio)phenyl cation immediately after its formation. The estimated activation barrier for this reaction is only 0.48 kcal/mol. At the same time, the gain in energy is significant and exceeds 107 kcal/mol (Fig. 4).

Meanwhile, the transition state **TS4** corresponds to the reaction of 2-(iminomethoxy)phenyl cation and characterizes by the same torsion angle  $\tau$  being equal to 102.2°. When the reaction is proceeding toward the reagent, the  $\tau$  increases up to 132.5° at the stationary point  $s = -2.06$  amu<sup>1/2</sup> Bohr. In contrast, the formation of benzo[*d*]oxazol-3-ium is finished at  $s = 21.18$  amu<sup>1/2</sup> Bohr. Thus, the shape of the IRC is close to that of 2-(iminomethylthio)phenyl cation. The barrier of activation is even smaller than in the case of 2-SCH=NH and equal to 0.25 kcal/mol, whereas the releasing energy is about 103 kcal/mol.

Summarizing, for the both 2-(iminomethylthio)phenyl and 2-(iminomethoxy)phenyl cation the ring closure reaction efficiently occurs. Thermodynamically, both these are exothermic with the releasing energy higher than 100 kcal/mol. The transition states have been found to lie close to the aryl precursors in the both thermodynamic and kinetic aspects.

### 3.3. Ortho-nitrophenyl cation reaction pattern

The B3LYP/6-31G(d,p) geometry optimization of 2-nitrophenyl cation in the singlet state provides a quite unusual result. The structure obtained with this approach is shown in Fig. 5, A. Change of the basis set up to the 6-311G(d,p) as well as addition of the diffusion functions give the same rearranged structure (RS). Meanwhile, the Hartree-Fock (HF) method and the second-order Møller-Plesset perturbation method (MP2) locate the global minimum for a not rearranged structure, which exists in a form of the aryl cation. Certainly, it is difficult to interpret such the quite dif-

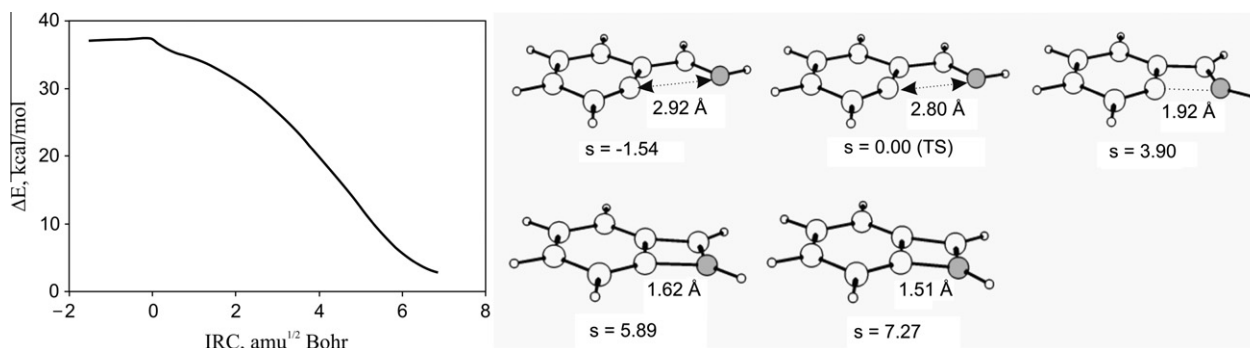


Fig. 3. Potential energy profile connecting 2-(iminomethyl)phenyl cation with benzo[*b*]azetium together with geometry transformation along the IRC.



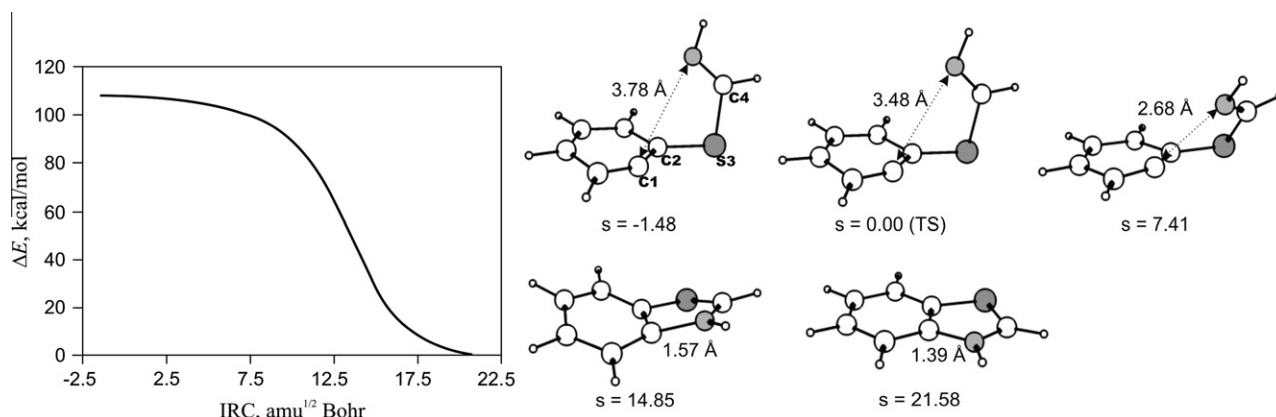


Fig. 4. Potential energy profile of the ring closure reaction of 2-(iminomethylthio)phenyl cation and geometry transformation along the IRC.

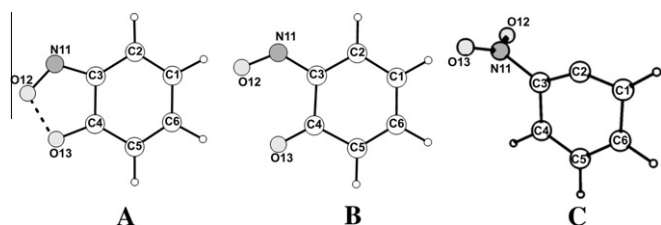


Fig. 5. The B3LYP optimized structure of 2-nitrophenyl cation in the gas phase for the both singlet (A), triplet (B) and singlet transition (C) states.

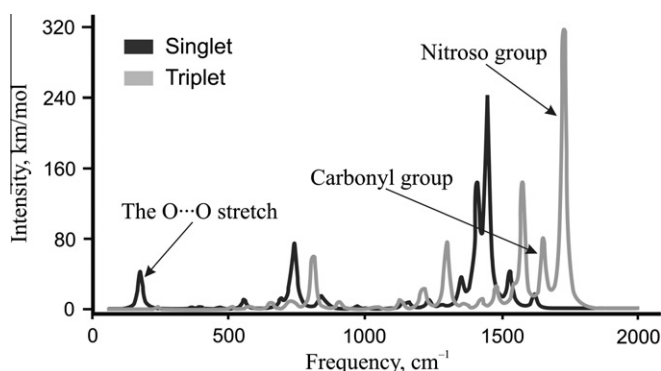


Fig. 6. IR spectra of the rearranged structure obtained by the optimization of 2-nitrophenyl cation in the gas phase with the B3LYP/6-31G(d,p) approach.

ferent structure results obtained by utilization of the various approaches.

At first glance, one can think that the RS (Fig. 5, A) has the carbonyl and nitroso group. But we have calculated the infrared (IR) spectrum of this cation in order to check the functional groups present. The analysis of the obtained IR spectrum of the RS shows that there is no simple carbonyl and nitroso group present in the singlet state, whereas the triplet state has intensive bands at 1641 and 1718  $\text{cm}^{-1}$  corresponding to the carbonyl and nitroso groups, respectively (Fig. 6). The singlet state of RS characterizes by a weak binding between the two oxygen atoms (O–O bond distance is equal to 1.665 Å). It is also reflects in the IR spectrum by occurrence of low-frequency band at 224  $\text{cm}^{-1}$ , which has the nature of the O–O stretch (Fig. 6).

Such the weak binding has a small force constant resulting in occurrence of the low-frequency band. It should be noted that the triplet excited state of the RS has been calculated with the starting rearranged geometry of the corresponding singlet. When

the triplet state optimization is performed starting from the geometry which corresponds to the aryl cation, the B3LYP/6-31G(d,p) method locates a minimum (symmetry  $C_s$ ) with the C–N bond length being equal to 1.48 Å and the N–O bond lengths being equal to 1.23 and 1.22 Å, respectively. A local minimum we have found for the singlet 2-nitrophenyl cation, when the dihedral angle  $\tau[C(2)-C(3)-N(11)-O(12)]$  has been equal to 90° (symmetry  $C_s$ ) with one imaginary frequency ( $-65 \text{ cm}^{-1}$ ) corresponding to the transition state (Fig. 5, C).

Optimization of geometry of 2-nitrophenyl cation in acetonitrile medium leads toward the not rearranged structure for the both singlet and triplet states. Surprisingly, the singlet–triplet ( $S \rightarrow T$ ) energy gap has been estimated to be equal to 11.3 kcal/mol. It is not characteristic for the aryl cations containing strong electron-withdrawing substituents, like the nitro group, because the above value lies in the range, which is close to that of 4-bromophenyl cation (9.3 kcal/mol). Despite the lower electron acceptor force, however, the  $S \rightarrow T$  energy gaps for the 2-CHO, 2-SO<sub>3</sub>H and 2-CH=NH has been calculated to be 19.3, 15.8 and 14.2 kcal/mol, respectively.

In order to confirm that 2-nitrophenyl cation rearranges into the RS, we have tried to obtain the corresponding TS. Unfortunately, no any TS connecting these two structures have been found. Scan of the PES for the obtained one, displays that this corresponds to the simple N–O bond rotation. As the reaction coordinate reached  $-5.39 \text{ amu}^{1/2} \text{ Bohr}$ , the curvature of PES became more declivous suggesting the optimized geometry. This structure must be considered as a transient occurring after the decay of the corresponding precursor (diazonium cation, 1-chloro-2-nitrobenzene or other source) and characterizes by the torsion angle  $\tau[C(2)-C(3)-N(11)-O(12)]$ , which is equal to 37°. The energy difference between formally existing singlet 2-nitrophenyl cation and the RS has been estimated to be 65.2 kcal/mol. Thus, it becomes obvious that 2-nitrophenyl cation and the RS lie on different PESs and there is no any reaction path leading from one structure to another. All the contradictory structural data obtaining from our calculations of 2-nitrophenyl cation together with ambiguous experimental results concerning its reactivity [18] have lead us to the fundamental conclusion about the impossibility of existing of the letter in the singlet spin state.

Milanesi et al. showed that during the photolysis of 4-nitrobenzenediazonium tetrafluoroborate in MeCN, the aryl cation is formed in part or completely in the triplet state [3]. Meanwhile, the electron-releasing substituents (*viz.* 4-(*tert*-Bu, 4-NMe<sub>2</sub>) as well as the parent phenyl cation, result in formation of the aryl cations in the singlet state. Based on the above experimental facts, we have modeled the photodecay of 1-chloro-2-nitrobenzene, which can be utilized as the analogue to 2-nitrobenzenediazonium tetra-

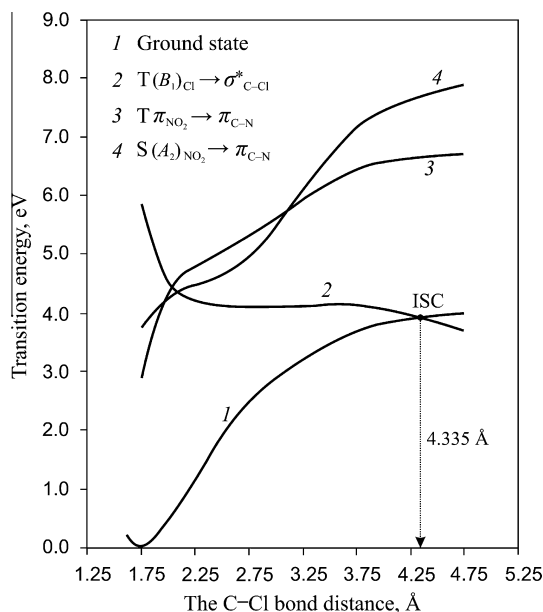


Fig. 7. Energy of the ground and excited states of 1-chloro-2-nitrobenzene at different the C–Cl bond distances.

fluoroborate. In these calculations, the geometry has been optimized at each point with single step of 0.5 Å. The calculations have been performed in acetonitrile medium, which is suitable for modeling of the heterolysis of the C–Cl bond, rather than homolysis.

At the equilibrium point, which corresponds to the C–Cl bond length being equal to 1.750 Å (*singlet*) and 1.755 Å (*triplet*), the energy difference between these two states is equal to 54.7 kcal/mol. As a chloride ion moves away from the carbon atom the  $S \rightarrow T$  energy gap is remaining to be almost the same, up to 2 Å. Further detachment of the  $\text{Cl}^-$  ion is accompanied by a smooth diminishing of the  $S \rightarrow T$  energy gap and the intersystem crossing (ISC) occurs when the chloride ion becomes distant to 4.335 Å. The system requires about 106.2 kcal/mol to overcome the energetic barrier.

To understand the nature of the transitions leading to the triplet state formation of 1-chloro-2-nitrobenzene, we have performed TD DFT calculations of the letter at different the C–Cl bond distances. Fig. 7 displays the obtained curves. As it can be seen in Fig. 7, the curve 1 reflects the ground state of 1-chloro-2-nitrobenzene molecule. Its energy rises gradually up to the complete dissociation. The first triplet excitation (curve 3) is an electron transition from the  $\pi$ -type MO localized on the nitro group to the lowest unoccupied molecular orbital (LUMO), which is also of the  $\pi$ -type with the bonding character along the C–N link. We have abbreviated these

as the  $\pi_{\text{NO}_2}$  - and  $\pi_{\text{C-N}}$  -MO, respectively. The fourth curve is the first singlet excitation from the MO, which is similar to the  $A_2$  MO in chlorobenzene molecule (symmetry  $C_{2v}$ ) with contribution from the nitro group (denoted as  $(A_2)_{\text{NO}_2}$ ) to the LUMO. Finally, the second curve is the most high-energetic transition and it has been marked as  $T(B_1)_{\text{Cl}} \rightarrow \sigma_{\text{C-Cl}}^*$ . The  $(B_1)_{\text{Cl}}$  MO is the highest occupied molecular orbital (HOMO) of 1-chloro-2-nitrobenzene molecule, which has similar nature to the  $B_1$  MO of chlorobenzene with only difference that it includes the chlorine atom instead of the H-atom. The  $\sigma_{\text{C-Cl}}^*$ -MO is the  $\sigma$ -type orbital with antibonding character along the C–Cl link. The electron skipping onto the  $\sigma_{\text{C-Cl}}^*$ -MO results in weakening of the C–Cl bond and subsequent facilitating the chloride anion detachment. When the C–Cl bond is completely cleaved the  $\sigma_{\text{C-Cl}}^*$ -MO transforms into the  $\sigma$ -type MO of the corresponding aryl cation (Fig. 8, MO 32) and the chloride ion MO. We have shown former that the detachment of a nitrogen molecule from a diazonium cation is proceeding through the same type transition that of  $T(B_1)_{\text{Cl}} \rightarrow \sigma_{\text{C-Cl}}^*$  [39]. Such similarity between the aryl diazonium salts and chloroarenes in the nature of the MOs and electron excitations defines these reagents as efficient sources of the aryl cations in photochemical and thermal reactions [1–3,13,39].

At the equilibrium point, the  $T(B_1)_{\text{Cl}} \rightarrow \sigma_{\text{C-Cl}}^*$  transition requires more than 5.5 eV of energy (Fig. 8), but with elongation of the C–Cl bond, its energy falls down sharply to 4 eV keeping this value up to 3.75 Å. Further elongation of the C–Cl bond causes a subsequent decrease of the excitation energy and at 4.335 Å the intersystem crossing (ISC) occurs resulting in change of the formed aryl cation spin multiplicity. The  $S \rightarrow T$  transition in 2-nitrophenyl cation is proceeding due to the SOC effect, which has been described former in Ref. [20]. In the parent phenyl cation, one can observe the rotation of a spin around one center providing  $\pi \rightarrow \sigma$  transition. Harvey et al. calculated the SOC matrix element for the parent phenyl cation to be 5.8  $\text{cm}^{-1}$  using an approximate one-electron operator [5]. We have repeated this calculation and obtained the value being equal to 5.1  $\text{cm}^{-1}$ . Despite such a small coupling energy it is very important and large enough to provide the  $S \rightarrow T$  transitions in similar systems [40].

The wavefunctions of 2-nitrophenyl cation have been expanded within the CASSCF method, the active space being comprised of 10 electrons in 10 orbitals. The ground singlet state is characterized by the closed electron shell with negligible contributions of different configurations. The calculated singlet and triplet states of 2-nitrophenyl cation are shown in Fig. 8. The  $S_1 \rightarrow T_1$  SOC matrix element is nonzero and equal to 1.42  $\text{cm}^{-1}$ . These two spin states lie very closely to each other with the energetic difference being equal to 11.3 kcal/mol. Such the pattern is peculiar for the aryl cations having electron releasing substituents in the aromatic nucleus. Surprisingly, the  $S_1 \rightarrow T_1$  transition is proceeding from the  $\text{MO}_{30}$

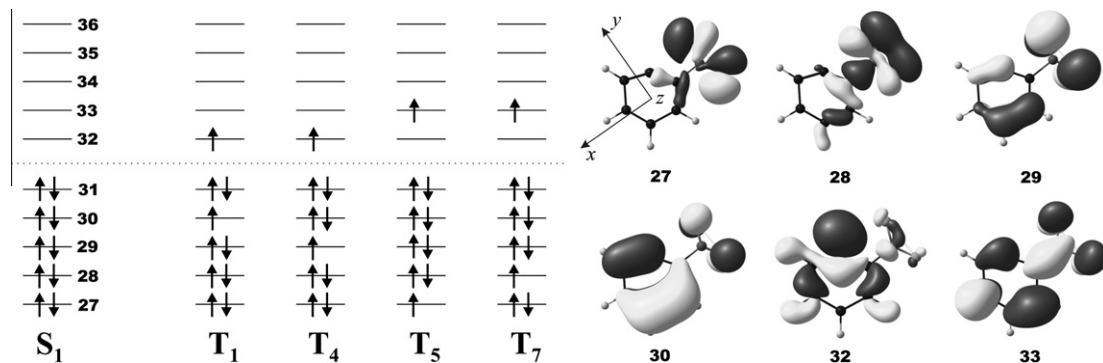


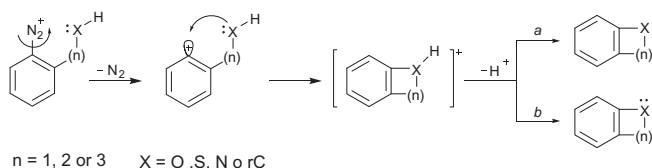
Fig. 8. Configurations of the ground singlet and excited triplet states of 2-nitrophenyl cation together with molecular orbitals, which are involved in the transitions.

to the  $\text{MO}_{32}$ , not from the highest occupied  $\text{MO}_{31}$ . The  $\text{MO}_{30}$  is occupied  $\pi$ -orbital with contribution from the nitro group ( $p_z$  orbitals of the oxygen atom). On the other hand, the  $\text{MO}_{32}$  is the sigma type orbital with major contribution on hydrogen free carbon atom. A simple spin rotation around the  $x$  and/or  $y$  axis provides change of the spin orientation and causes the SOC.

The  $S_1 \rightarrow T_4$  transition requires 110.0 kcal/mol of energy, but it is accompanied by the relatively strong SOC having the matrix element being equal to  $14.8 \text{ cm}^{-1}$ . Like the above case, now we have the  $\pi \rightarrow \sigma$  transition with major contribution from the nitro group. In contrast, the other transitions ( $S_1 \rightarrow T_5$  and  $S_1 \rightarrow T_7$ ) are of the  $\sigma \rightarrow \pi$  type. Occupied MOs 27 and 28 lie in plane of the cation and are the  $p_y$  and  $p_x$  orbitals of the oxygen atoms, respectively. The  $S_1 \rightarrow T_5$  transition is of only 1 kcal/mol higher than the  $S_1 \rightarrow T_4$  one, but it is much more intensive because it has the SOC matrix element being equal to  $49.3 \text{ cm}^{-1}$ . Finally, the  $S_1 \rightarrow T_7$  transition is the highest energetic ( $115.4 \text{ kcal/mol}$ ), however, it has also comparatively strong the SOC matrix element being equal to  $8.4 \text{ cm}^{-1}$ .

#### 4. Conclusion

Using density functional theory calculations, the structural properties and some aspects of the *ortho*-substituted phenyl cations reactivity have been studied. For the cations **1–7**, the simple ring closure gas phase reaction has been suggested. Moreover, the cations **3, 5–7** can also form the cycles in MeCN medium, as it follows from our DFT/B3LYP/6-31G(d,p) calculations. For several examples of the ring closure reaction, the corresponding transition states have been found to be reactants-like in the both kinetic and thermodynamic aspects. Basing on the results of the calculations, the following general scheme of the ring closure reaction has been offered.



Calculations have shown that the singlet state of 2-nitrophenyl cation cannot exist in the gas phase. When it is formed under such conditions, it has the triplet ground state which has been found to be stable enough. The possibility of the  $S \rightarrow T$  transitions is due to the SOC effect. For 2-nitrophenyl cation, the SOC matrix element has been found to be  $1.42 \text{ cm}^{-1}$ , suggesting the relatively long lifetime for this triplet spin state.

Obviously, the above gas phase generation of *ortho*-substituted phenyl cations can also be performed using the electron beam im-

pact. Thus, the mass spectroscopic study of these cations is of great interest for further investigations.

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