

A DFT Study on the Nucleophilic Substitution of NO₂-Group in 2-Nitrophthalocyanines

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The reaction of NO₂-group nucleophilic substitution in mononitrophthalocyanines has been studied using quantum-chemical calculations (DFT//PBE/TZ2P). The reaction is shown to proceed through the ipso-complex formation due to negligible energetic barrier (0.2 kcal/mol) of the transition state on the 2-σ-complex → products route.

Keywords: Phthalocyanine, nucleophilic substitution, ipso-complex, DFT.

Introduction

Phthalocyanines are the conjugated heterocyclic compounds containing isoindoline rings connected through sp²-hybridized nitrogen atoms.^[1] The interest to these macroheterocyclic compounds arises from their structural similarity with widely spread porphyrins. Due to their high chemical and thermal stability as well as intensive absorption in the visible (ε~10⁵ M⁻¹ cm⁻¹) and near IR regions,^[2-4] phthalocyanines are applied as new perspective materials, mainly, in molecular electronic devices,^[1] as optical recording materials,^[5] catalysts for conversion of pollutants to useful products,^[6-8] sensitizers for PDT^[9,10] and antiviral chemicals.^[11,12]

A considerable interest of scientists is directed to the asymmetrically substituted monophthalocyanines of A₃B-type bearing one peripheral functional substituent or fragment.^[13] Due to this peculiarity a further structural modification is possible, resulting in a number of unique building-blocks for preparation of nanosized polynuclear macromolecules.^[14-16] Earlier we have shown a possibility of nucleophilic substitution of the NO₂-group in mononitrophthalocyanines, which was used for preparation of asymmetrically substituted monophthalocyanines containing benzyl alcohol fragment.^[17] In the present work an attempt of theoretical quantum-chemical study of the mechanism of this reaction is undertaken to establish the structure of the intermediate anionic σ-complex.

Experimental

Calculations

Quantum-chemical calculations were performed using density functional theory (DFT) method. The Perdew–Burke–Ernzerhof (PBE)^[18] functional and PRIRODA 08 package^[19] supplied with three exponent TZ2P basis set including twice polarized Gauss-type functions were used for optimization of the structural geometries corresponded to steady and transition states. The size of the basis set used is - (11s6p2d):[6s3p2d] for C and N, (5s1p):[3s1p] for

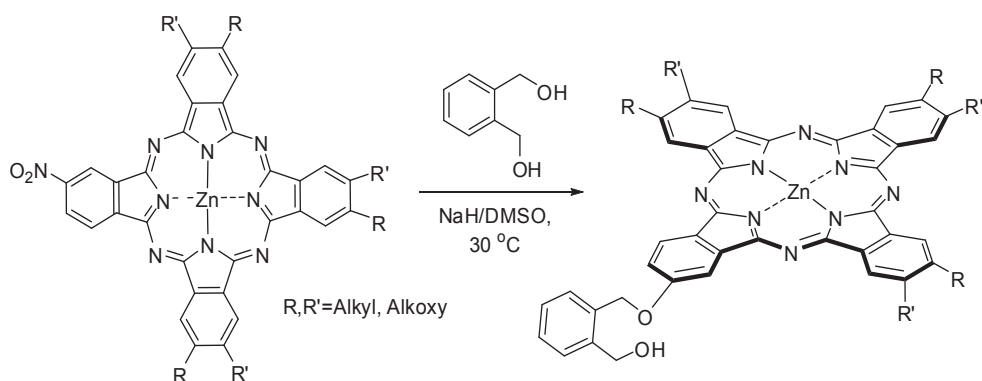
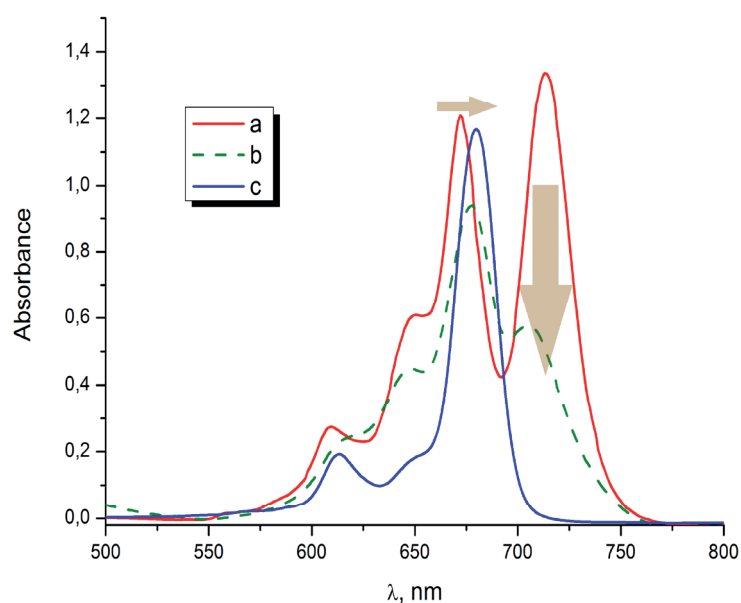
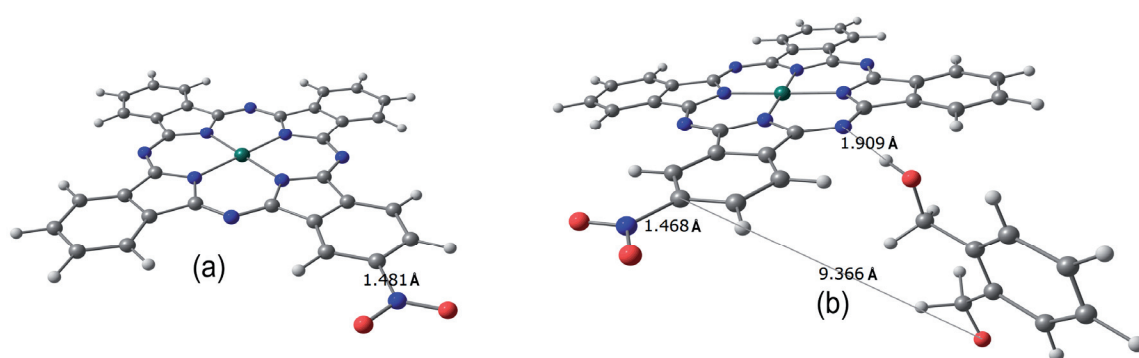
H and (17s13p8d):[12s9p4d] for Zn atoms. The PBE functional is very satisfactory from the theoretical point of view because it does not contain any fitting parameters. Due to this feature the binding energies, geometries and dynamical properties of different molecules calculated with the PBE functional show the best agreement with experiment.^[20] The calculation of thermodynamic values were also done with B3LYP^[21,22] functional and 6-31G(*d,p*) basis set encapsulated into GAMESS-US^[23] program package. This combination of calculation procedures reproduces experimental results with high accuracy.^[24]

Results and Discussion

Despite of an obvious priority of experimental investigations in chemistry, the role of molecular modelling is high enough. Theoretical results are the most meaningful in the cases when experimental way is impossible, extremely difficult or expensive. Traditionally calculations are used for the investigation of the unstable molecules and molecular associates which is necessary to reveal the chemical reaction mechanisms on the molecular level.^[25]

The investigation of nucleophilic substitution reaction of NO₂-group by benzyl alcohol fragment (Scheme 1) using UV-vis spectroscopy (Figure 1) allowed us to make some assumptions concerning smooth course of process.^[26]

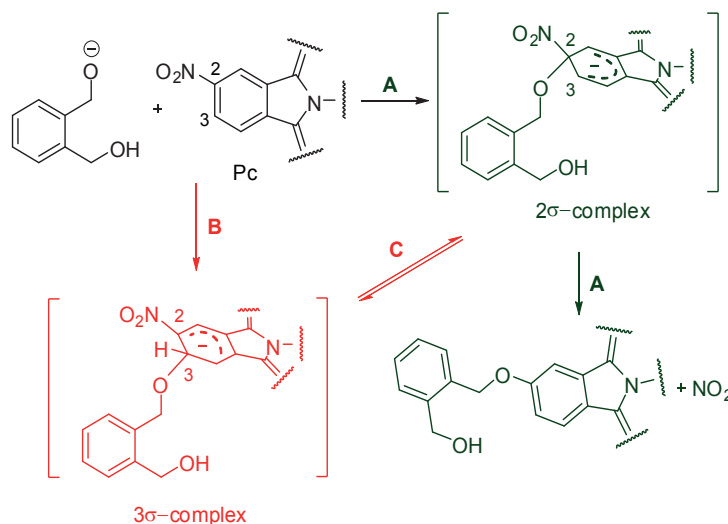
Thus, it is possible to establish high reactivity of the intermediate form (σ⁻-complex) in the real conditions. Proceeding from the general concepts, one may consider that the nucleophilic attack and nitro-group elimination occur synchronously at first approximation, *i.e.* anionic 2σ⁻-complex which is structurally similar to Meisenheimer's one, is formed as an intermediate. However it is possible to propose an alternative route for the reaction process (Scheme 2). It includes formation of an anionic 3σ⁻-complex followed by migration of benzyl alcohol fragment (route B-1) or H-anion as well (route B-2). The last, most likely, can not take place in practice, as the reaction mixture has no strong oxidizers. Therefore in this connection we will consider only theoretical possibility of B-2 route to compare it with other routes.

**Scheme 1.** Nucleophilic substitution of NO_2 -group.**Figure 1.** Changes of UV-vis spectra (DMSO) during the substitution of nitro-group according to Scheme 1: a - initial zinc(II) complex of 2-nitro-9,10,16,17,23,24-hexabutylphthalocyanine, b - reaction mixture after 30 min, c - target product.**Figure 2.** DFT optimized structures of starting 2-nitrophthalocyanine (a) and reaction complex RC (b).

The mechanism of nucleophilic substitution of the nitro group in 2-nitrophthalocyanines was studied using quantum-chemical calculations. The structure of non-substituted 2-nitrophthalocyanine zinc complex was used as a model for such investigation. This approach simplifies the calculations and reduces the computation time. First, a total geometry optimization of starting compounds –

substrate, nucleophile and reaction complex – was carried out (Figure 2).

Analysis of a potential energy surface (PES) during possible ways of the reaction course (A and B, Scheme 2) included step-by-step rapprochement of reagents (with accuracy 0.1 Å) until formation of intermediates (2- σ - or 3- σ -complexes). The following optimization of the 2- σ -



Scheme 2. Theoretically possible ways of NO₂-group substitution reaction in mononitrophthalocyanines.

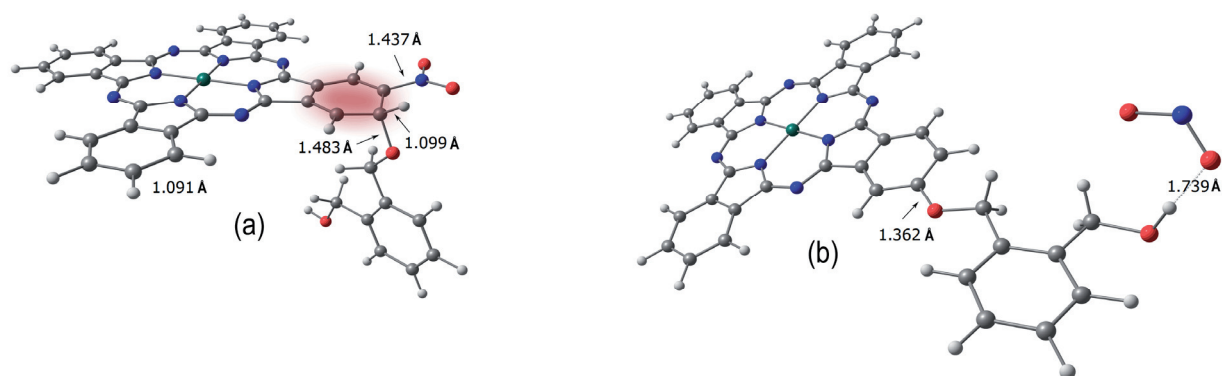


Figure 3. DFT optimized structures of 3- σ -complex (a) and products complex PC (b).

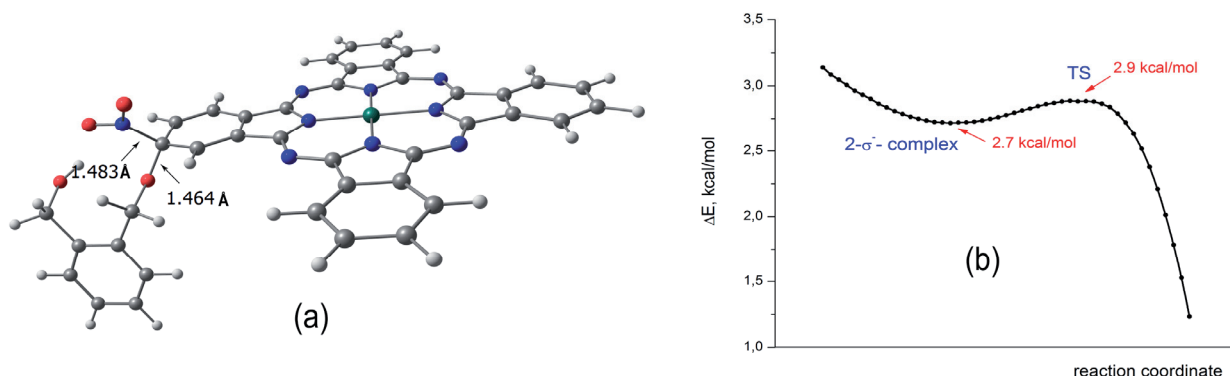


Figure 4. DFT optimized structure of 2- σ -complex (a) and IRC scanning of its transformation to products (b). The total energy change relative RC is shown on ordinate axis.

complex geometry found during scanning of the PES results in the products formation; whereas 3- σ -complex has the steady geometry with insignificant distortion of a benzene ring plane including the nitro-group (Figure 3).

Increase of a scanning precision by order (0.01 Å) lets us to find the transition geometry during the transformation of the 2- σ -complex (route A, Scheme 2). Total energy change in the reaction course during the formation of the activated complex was 0.2 kcal/mol (Figure 4) indicating that the

ipso-substitution of nitro group follows the synchronous mechanism, which is in agreement with large amount of experimental data.

In the study of the 2- $\sigma \leftrightarrow$ 3- σ complex transformation process the PES scanning was carried out by rapprochement of oxygen atom in the 3- σ -complex structure with carbon atom connected with the nitro group to obtain the 2- σ -complex (route C, Scheme 2). The transition state is shown to be substantial higher ($\Delta E = 14.8$ kcal/mol) revealing

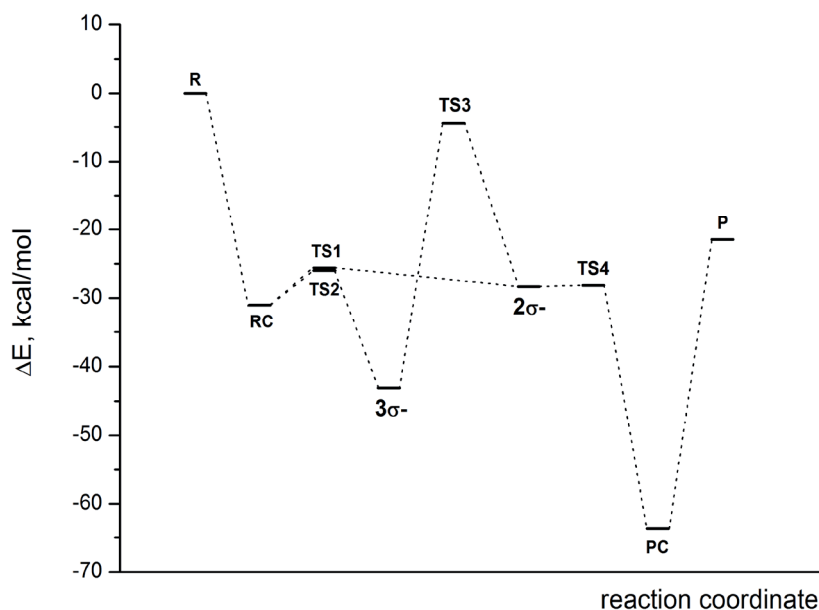


Figure 5. Total energy changes during nucleophilic nitro group substitution. R – reagents, RC – reaction complex, TS1 and TS2 – activated complexes in the course of the 2- σ^- - and 3- σ^- -complexes formation, TS3 and TS4 – activated complexes in the course of the following transformation of the 3- σ^- - and 2- σ^- -complexes, PC – products complex, P – products.

that this route is less probable in comparison with the 2- σ^- -complex formation and its further transformation. Figure 5 shows the total energy change in the investigated routes.

All of the states shown in Figure 5 are stationary points on PES; RC, 2- σ^- - and 3- σ^- -complexes as well as PC are local minima, transition states TS1-TS4 have strictly by one imaginary frequency in Hessian. For IRC scanning, the structure correspondence to transition states has been optimized as saddle points. As follows from Figure 5, energy of transition states (TS1 and TS2) during formation of 2- σ^- - and 3- σ^- -complexes are close, however the energy barriers of their further transformation are essentially different, indicating that traditional synchronous process (route A) is more preferable. At the same time, high stability of 3- σ^- -complex could force the reaction break, and in this case the intermediate could be isolated or, at least, fixed by UV-vis spectroscopy. However it was not observed in practice.

The obtained quantum-chemical calculations results are performed for a gas phase. The account of a solvent presence (DMSO, model PCM in program complex GAMESS-US) led to the minor alteration of geometrical parameters, total energy and thermodynamic values. It does not affect the general picture of theoretically possible routes for the nucleophilic reaction under investigation.

Conclusions

Application of DFT method let us to conclude our reaction proceeds through the formation of *ipso*-complex as an intermediate. The result obtained is caused by a high activating influence of phthalocyanine macrocycle. Insignificant influence of solvent on the calculated thermodynamic values was established.

Acknowledgements. We thank I.P. Gloriov (Moscow State University, Chemistry Department) for consultations

while carrying out the quantum-chemical calculations as well as JSCC RAS (www.jscc.ru) for the given computing resources.

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Received 06.12.2010

Accepted 31.01.2011