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*A.I. Karkhut, S.V. Polovkovych, M.S. Kurka, L.R. Zhurakhivska, V.P. Novikov***DFT STUDY OF CHARGE TRANSFER ASSISTED DIELS-ALDER REACTION OF AZO-BIS-2,4-DICHLORO-1,3,5-TRIAZINE AND ANTHRACENE**

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Diels-Alder reaction of anthracene and its derivatives with various dienes are of great interest as it is used in many branches of chemistry: from synthesis of biologically active substances to dendrimers extension. In this study, we considered a rapid irreversible Diels-Alder reaction between anthracene and azo-bis-cyanuric chloride as active electron-deficient diene which can be easily functionalized. The investigation was performed experimentally and on M06-2X/6-31+G(d,p) level. It was found that the reaction proceeds through the formation of intermediate colored charge transfer complex which is rapidly exhausted. The reaction was found to be synchronic with symmetric transition state and charge transfer ratio about 0.56 electron. The conditions of a further modification of the product by chlorine atoms substitution were also determined. It rapidly decomposes in strong acidic medium but is stable thermally and in alkaline conditions, which makes it possible to modify it further by different nucleophiles. The O- and N-substituted compounds were obtained via the reaction of Diels-Alder reaction product with sodium alcoholates at room temperature and with secondary amines at 90°C in the presence of triethylamine, respectively. The structure of products was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The charge transfer bands of intermediate complex were characterized by UV-Vis spectroscopy.

**Keywords:** azo-bis-4,6-dichloro-1,3,5-triazine, anthracene, DFT calculations, Diels-Alder cycloaddition, donor-acceptor complex.

**Introduction**

Diels-Alder reaction is widely used in organic syntheses since it provides the one-stage formation of a variety of six-membered carbo- and heterocycle from dienes and dienophiles [1]. Azo-compounds belongs to active dienophiles, especially with strong electron-withdrawing substituents (for instance, dichloro-1,3,5-triazine moiety). Azo-bis-2,4-dichloro-1,3,5-triazine has been synthesized and described as an active aza-dienophile in the reaction with 1,3-carbodienes with the formation of different substituted pyridazines [2], but its reactions with other conjugated systems have not been investigated yet. Despite its aromaticity, the possibility of the behavior of anthracene as diene both under thermal and photochemical conditions is well-known and widely used in organic synthesis. It can easily undergo the addition of electron-deficient unsaturated bonds in 9 and 10 position forming bridged systems [3]. The Diels-Alder reaction of anthracene as well as its derivatives and a variety of dienes, such as maleic anhydride [4], maleimide [5], acrolein [6] and tetracyanoethylene (TCE) [7], is well-known; its

mechanism and selectivity were investigated by experimental and computational methods. It is used in the construction of dendrimers to add different functional groups on their periphery [8], in “click” chemistry [9] and in the synthesis of a variety of compounds: from fluorescent sensors [10] to biologically active substances [11]. The reaction of anthracene and its derivatives with azo-bis-cyanuric chloride can be of great interest since its chlorine atoms are reactive and can be easily substituted by different nucleophiles, which can be used in modification of compounds properties or in further elongation of dendrimers.

In this work, the Diels-Alder reaction of unsubstituted anthracene and azo-bis-cyanuric chloride was studied experimentally and on DFT level; the conditions of further chlorine atoms substitution were determined too.

**Experimental**

All chemicals were purchased from Aldrich Chemical Company (USA) and were used without any purification. Azo-bis-4,6-dichloro-1,3,5-triazine was obtained by cyanuric chloride reaction with

hydrazine with subsequent oxidation by chlorine gas as described elsewhere [2]. The reactions were monitored by precoated aluminum silica gel 60F 254 thin layer plates (TLC analysis) procured from Merck (Germany) with chloroform – ethyl acetate eluent (2:1). The nuclear magnetic resonance ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) spectra were recorded in deuterated chloroform ( $\text{CDCl}_3$ ) with «Varian Mercury» (400/125 MHz) NMR spectrometer, chemical shifts are expressed in  $\delta$  parts per million (ppm) and reported relative to the solvent signal. Coupling constants were reported in Hz (s: singlet, bs: broad singlet, d: doublet, t: triplet, dd: double doublet, q: quartet, m: multiplet).

#### Computational details

All reported geometries, energies and rotation barriers were calculated using hybrid M06-2X [12] functional with 6-31+G(d,p) basis set included in the GAUSSIAN 09 Rev.01B [13] program using PCM solvation model (dichloromethane). First-order saddle point was localized using the standard procedure starting from geometry obtained from PES scan. For optimized structures, the confirmation of their nature and thermochemical data were obtained using vibrational analysis on the same level of theory. The UV-Vis spectra were calculated using TD-DFT on the same level of theory. The Gibbs free energies were used to discuss transition states and products stability. The global reactivity indices of reactants were calculated in terms of the one-electron energies of the frontier molecular orbitals according to the equations recommended by Parr and Domingo [14,15] on B3LYP/6-31G(d) level.

#### 11,12-bis(4,6-dichloro-1,3,5-triazin-2-yl)-9,10-dihydro-9,10-diazanoanthracene (4)

The anthracene (2) powder (0.274 g, 1.54 mmol) was added to the stirred solution of 0.5 g (1.54 mmol) of azo-bis-cyanuric chloride (1) in 10 mL of dichloromethane at room temperature. The color of solution gradually changed from deep red to light green and within 10 minutes a colorless solution was formed. It was then filtered through thin silica gel layer and the solvent was evaporated in vacuum. The product (0.71 g) was obtained as a colorless powder with a yield of 92%.  $R_f=0.61$ ; m.p. 167–168°C;  $^1\text{H}$  NMR (400 MHz,  $\delta$ , ppm): 7.47 (2 H, t,  $J=4.1$  Hz), 7.39 (2 H, t,  $J=4.2$  Hz), 7.16 (4 H, t,  $J=4.2$  Hz), 6.97 (2 H, s);  $^{13}\text{C}$  NMR (125 MHz,  $\delta$ , ppm): 171.2 (C); 170.2 (C); 141.6 (C); 134.8 (C); 128.4 (CH); 128.0 (CH); 126.2 (CH); 123.2 (CH); 61.5 (CH); Found, %: C 47.62, H 2.06, N 22.20, Cl 28.05. Calculated, %: C 47.65, H 2.00, N 22.23, Cl 28.13.

#### 11,12-bis(4,6-dimethoxy-1,3,5-triazin-2-yl)-9,10-dihydro-9,10-diazanoanthracene (5.1)

M MeONa solution in methanol (4 mL, 12 mmol MeONa) was slowly added to the stirred and cooled in ice bath suspension of 11,12-bis(4,6-dichloro-1,3,5-triazin-2-yl)-9,10-dihydro-9,10-diazanoanthracene (4) (1 g, 1.98 mmol) in 10 mL of methanol. The temperature was maintained at 5–10°C. 10 minutes later, the suspension was diluted with ice water (50 mL), the precipitate was filtered, washed with ice water until neutral, dried in vacuum over  $\text{CaCl}_2$  and reprecipitated from acetone/hexane. White powder was obtained with a yield of 78%.  $^1\text{H}$  (400 MHz,  $\delta$ , ppm): m.p. 172–173°C; 7.36 (2 H, t,  $J=4.2$  Hz), 7.29 (2 H, t,  $J=4.3$  Hz), 7.11 (4 H, t,  $J=4.2$  Hz), 6.73 (2 H, s), 4.00 (6 H, s), 3.86 (6 H, s); Found, %: C 59.20, H 4.63, N 22.96. Calculated, %: C 59.25, H 4.56, N 23.03.

11,12-bis(4,6-diethoxy-1,3,5-triazin-2-yl)-9,10-dihydro-9,10-diazanoanthracene (5.2) Was obtained similarly in reaction with EtONa with a yield of 75%. m.p. 178–179°C;  $^1\text{H}$  (400 MHz,  $\delta$ , ppm): 7.31 (2 H, t,  $J=4.2$  Hz), 7.25 (2 H, t,  $J=4.1$  Hz), 7.08 (4 H, t,  $J=4.1$  Hz), 6.68 (2 H, s); 4.31 (8 H, m), 1.42 (12 H, br. s); Found, %: C 61.93, H 5.49, N 20.57. Calculated, %: C 61.98, H 5.57, N 20.65.

#### 6,6'-(9,10-dihydro-9,10-diazanoanthracene-11,12-diyl)bis(N,N,N',N'-tetramethyl-1,3,5-triazine-2,4-diamine) (6.1)

The solution of dimethylamine (0.54 g, 12 mmol) and triethylamine (0.62 g, 7.7 mmol) in 5 ml of toluene was added to the solution of 11,12-bis(4,6-dichloro-1,3,5-triazin-2-yl)-9,10-dihydro-9,10-diazanoanthracene (4) (1 g, 1.98 mmol) in 5 mL of toluene. The solution was sealed into a glass ampoule and heated at 80–90°C for 2 hours, then cooled, washed with water (3×5 mL), dried with sodium sulfate and vacuum-evaporated. Slight-yellow oil that slowly hardened was obtained with a yield of 81%. m.p. (–);  $^1\text{H}$  (400 MHz,  $\delta$ , ppm): 7.13 (2 H, t,  $J=4.2$  Hz), 7.05 (2 H, t,  $J=4.3$  Hz), 6.53 (4 H, t,  $J=4.2$  Hz), 5.91 (2 H, s), 3.52 (12 H, br. s), 3.39 (12 H, br. s); Found, %: C 62.47, H 6.47, N 31.31. Calculated, %: C 62.43, H 6.36, N 31.20.

#### 6,6'-(9,10-dihydro-9,10-diazanoanthracene-11,12-diyl)bis(N,N,N',N'-tetraethyl-1,3,5-triazine-2,4-diamine) (6.2)

Diethylamine (0.448 g, 7.7 mmol) and triethylamine (0.620 g, 7.7 mmol) were added to the suspension of 11,12-bis(4,6-dichloro-1,3,5-triazin-2-yl)-9,10-dihydro-9,10-diazanoanthracene (4) (1 g, 1.98 mmol) in 10 mL of toluene. The solution was stirred and heated under reflux condenser at 80–90°C for 2 hours, then cooled, washed with water (3×5 mL), dried with sodium sulfate and vacuum-evaporated. Slight-yellow oil that

slowly hardened was obtained with a yield of 78%. m.p. (-);  $^1\text{H}$  (400 MHz,  $\delta$ , ppm): 7.10 (2 H, t,  $J=4.3$  Hz), 7.03 (2 H, t,  $J=4.2$  Hz), 6.47 (4 H, t,  $J=4.2$  Hz), 5.88 (2 H, s), 3.66 (8 H, m), 1.15 (12 H, br. s); Found, %: C 66.49, H 7.83, N 25.93. Calculated, %: C 66.43, H 7.74, N 25.82.

### Results and discussion

The reaction was studied in various solvents. It was stated that it can be performed in solvents which are inert in relation to azo-bis-cyanuric chloride at room temperature with a high yield; the reaction proceeds easily with the suspension of anthracene despite its low solubility. However, the best results were obtained with the use of more polar solvents, such as chloroform and DCM; it occurs in less polar benzene and toluene with a significant decrease in the reaction rate. It is due to a large differences in electrophilicity ( $\omega$ ) and nucleophilicity ( $\Delta N_{\text{max}}$ ) indices of reagents and, hence, a high reaction polarity (Table).

### Global reactivity indices of reacting molecules

Compound	HOMO, eV	LUMO, eV	$\omega$	$\Delta N_{\text{max}}$
Azo-bis-cyanuric chloride ( <b>1</b> )	-7.90	-3.92	4.39	1.05
Anthracene ( <b>2</b> )	-5.22	-1.89	1.90	3.73

In all used solvents, the reaction is accompanied by the appearance of green coloration which is especially noticeable on the surface of anthracene crystals. It becomes visible in bulk solution after reducing the concentration of deep-red azo-bis-cyanuric chloride. It was of interest to reveal the nature of this coloration.

We decided to study the reaction mechanism on DFT level using M06-2X as accurate functional for thermodynamic calculations. The calculated energy profile and Gibbs free energy differences for transition state and products are shown in Fig. 1.

It was found that the reaction starts with barrierless formation of coplanar charge transfer (CT) complex from reactants with calculated  $\Delta G = -2.2$  kcal/mol in DCM which is responsible for the above-mentioned appearance of green coloration; its geometry is shown in Fig. 2. This complex provides the most advantageous orientation for charge transfer and its geometry is obvious due to maximizing the overlap in complex of reagents frontier orbitals with maximum coefficients: azotriazine low-lying LUMO is almost completely localized on azo-bond and anthracene HOMO has a predominant location on

9 and 10 positions.

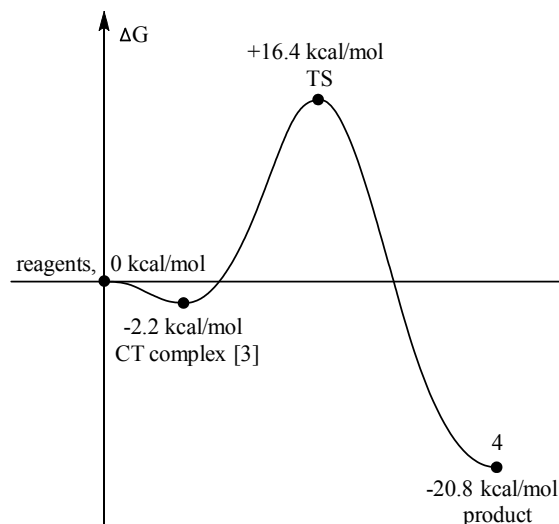


Fig. 1. DFT calculated energy profile of the reaction

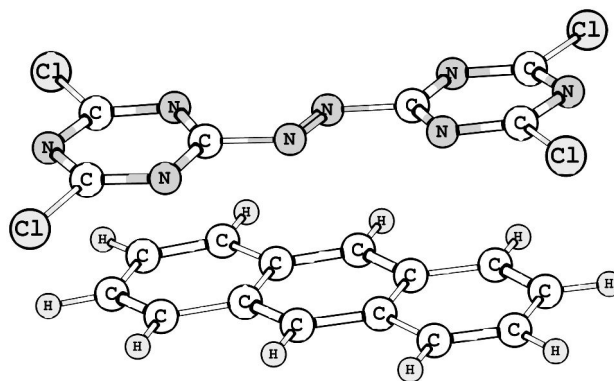


Fig. 2. M06-2X/6-31+G(d,p) calculated geometry of CT complex

The predicted electron donation from anthracene to azo-bis-cyanuric chloride in CT complex (from summation of components Mulliken atomic charges) is about 0.10 e confirming donor-acceptor component in this intermediate (partially anionic azo-cyanuric chloride and partially cationic anthracene). Both anthracene and azocyanuric chloride were predicted to be planar in complex, whereas azocyanuric chloride have triazine rings torsion angle of about 35 degrees due to 1,3,5-triazine cycle and azo-bond electronic pairs repulsion.

Since charge transfer complex cannot be isolated as an individual compound due to both its instability towards dissociation and its depletion in DA reaction, we obtained the UV-Vis spectra only

of the most long-wave absorption band (689 nm); it is well agreed with TD-DFT calculated data (676 nm). The band is corresponding to HOMO–LUMO charge transfer (anthracene→azo-bis-cyanuric chloride). The additional predicted CT band in the near-optical part of the spectrum, which mainly consists of HOMO–1 (also located on anthracene) – LUMO transition line (358 nm), is overlapping with azocyanuric chloride visible absorption band (439 nm).

Diels-Alder transition state geometry indicates synchronic one-step reaction with symmetric TS (both C–N distances of 2.19 Å). The reaction has a large polarity, its TS have a charge transfer of about 0.56 electron. The reaction mechanism is shown in Scheme 1.

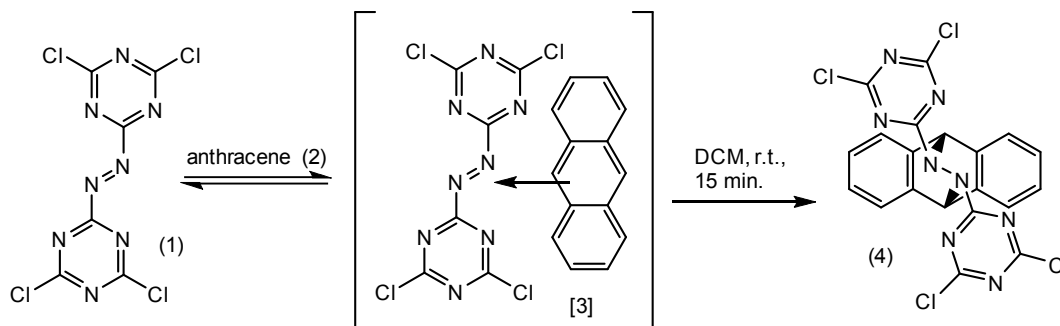
The obtained product can be easily functionalized by chlorine atoms nucleophilic substitution. As well as other previously studied azo-bis-cyanuric chloride DA products, the compound (4) was found to be instable in strong acidic medium. An attempt to substitute its chlorine atoms with methanol in acid catalysis conditions leads to N–N bridged system destruction, 4,6-dimethoxy-2-amino-1,3,5-triazine and anthracene being registered among its products by LC–MS. However, the compound skeleton was found to be stable in alkali medium, so chlorine atoms can be substituted with sodium alcoholates and with different amines at 80–90°C in

the presence of triethylamine. Methoxy (5.1) and ethoxy (5.2) tetra-substituted products as well as dimethylamino (6.1) and diethylamino (6.2) tetra-substituted products were obtained (Scheme 2).

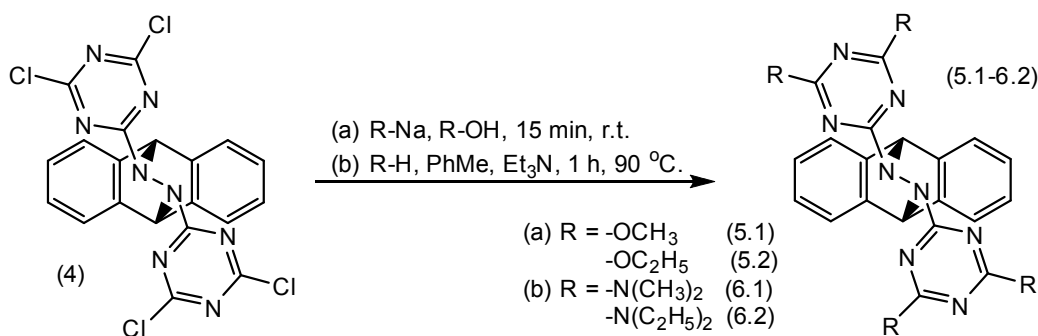
The structures of products were confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. In  $^{13}\text{C}$  spectra of product 3, the splitting of 4- and 6-triazazine carbon signals (about 1 ppm) is observed. The splitting of 4- and 6-methoxy groups  $^1\text{H}$  signal with  $\Delta\delta$  0.14 ppm is observed too, testifying hampered 1,3,5-triazazine cycles rotation and, hence, magnetic nonequivalence of medial and lateral nucleus. In cases of other substituted compounds, the signals broaden out and impede the manifestation of this effect.

### Conclusions

The Diels-Alder reaction between azo-bis-2,4-dichloro-1,3,5-triazazine and unsubstituted anthracene was investigated both experimentally in different solvents and theoretically on DFT level. It was found that the reaction starts with the formation of unstable intermediate donor-acceptor complex with M06 2X/6-31+G(d,p) calculated  $\text{DG} = -2.2$  kcal/mol and the charge transfer ratio of 0.10 electron. Its CT bands were characterized by UV–Vis spectroscopy and are well agreed with TD-DFT values. The reaction transition state with  $\Delta\text{G} = 16.4$  kcal/mol was found to be synchronic with large polarity (about 0.56 electron). The obtained product can be easily functionalized by O- and N- nucleophiles, so



Scheme 1



Scheme 2

methoxy-, ethoxy-, dimethylamino- and diethylamino- tetrasubstituted compounds were synthesized. The products structure was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

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#### DFT ДОСЛІДЖЕННЯ РЕАКЦІЇ ДІЛЬСА-АЛЬДЕРА АЗО-БІС-2,4-ДИХЛОРО-1,3,5-ТРИАЗИНУ З АНТРАЦЕНОМ З ПРОМІЖНИМ УТВОРЕННЯМ КОМПЛЕКСУ З ПЕРЕНЕСЕННЯМ ЗАРЯДУ

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Реакція Дільса-Альдера антрацену і його похідних з різними дієнами становить великий інтерес, оскільки використовується у багатьох галузях хімії – від синтезу біологічно активних речовин до нарощення дендримерів. У цій роботі була досліджена експериментально та на M06-2X/6-31+G(d,p) рівні швидко незворотна реакція між антраценом та азо-біс-ціанурхлоридом як активним електронодефіцитним дієном, що може бути легко функціоналізований. Було встановлено, що реакція протікає з проміжним утворенням забарвленого донорно-акцепторного комплексу, що швидко вичерпується. Розрахований перехідний стан симетричний з перенесенням заряду біля 0,56 e, що свідчить про велику полярність реакції. Також були досліджені умови подальшої модифікації продукту заміщенням атомів хлору. Було встановлено, що він швидко руйнується у кислому середовищі, однак досить стійкий термічно та у лужному середовищі, що відкриває шлях до його подальшої модифікації різними нуклеофілами. Реакцією продукту з алкоголятами натрію при кімнатній температурі та з вторинними амінами при 90°C були одержані O- та N заміщені продукти, відповідно. Будова речовин підтверджена даними  $^1\text{H}$  та  $^{13}\text{C}$  ЯМР спектроскопії; смуги перенесення заряду проміжного комплексу зафіксовані UV-Vis спектроскопією.

**Ключові слова:** азо-біс-2,4-дихлоро-1,3,5-триазин, антрацен, DFT розрахунки, реакція Дільса-Альдера, донорно-акцепторний комплекс.

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