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EXPERIMENTAL AND DFT STUDY OF AZO-BIS-CYANURIC CHLORIDE POLAR DIELS-ALDER REACTION WITH A NUMBER OF DIENES. WAYS OF FURTHER MODIFICATION OF THE OBTAINED PRODUCTS

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Abstract. The reaction of azo-bis-cyanuric chloride as strong electrophilic aza-dienophile in Diels-Alder cycloaddition with a number of dienes of different nucleophilicity, namely 2,3-dimethylbutadiene, 2-methylbutadiene and 1-acethoxybutadiene, was carried out and computationally analyzed on B3LYP/6-31G(d,p) level. Local and global reactivity indices, based on FMO theory, as well as TS geometries and activation energies were calculated. Reaction proceeds rapidly with high yields and in mild conditions. Ways of products further modification by chlorine atoms substitution were also studied. Compounds were found to be stable in alkaline conditions but rapidly decompose in the presence of acids.

Keywords: Diels-Alder reaction, DFT calculations, 1,3,5-triazine, conformational analysis.

1. Introduction

Diels-Alder reaction is one of the most convenient methods of six-membered rings synthesis due to a large variety of dienes and dienophiles that can be used [1, 2]. Azo-compounds containing conjugated electron-withdrawing groups are very active dienophiles in normal electron demand DA reaction forming pyridazine cycle [3]. Aza-dienophiles containing electron-deficient *sym*-triazine are of great interest because 1,3,5-triazine moiety is a useful binder that allows to combine different fragments in one molecule and to modify products properties forming wide range of biologically active compounds [4, 5]. Azo-bis-cyanuric chloride had been described as very active dienophile able to rapidly react with 1,3-dienes even at room temperature [6]. Nevertheless, the influence of reaction conditions and products reactivity were not studied, as well as the reaction was not studied by computational methods. Computational studies on DFT level to date are the most attractive for investigation of reactions thermodynamic parameters, conformational analysis and prediction of products spectral properties [7]. Nowadays they are quick enough to give an opportunity to carry out routine studies of molecules including up to 100 atoms on desktop computer in a reasonable time [8]. DFT-based indices and descriptors are successfully applied to predict reactivity and regioselectivity in Diels-Alder reactions [9, 10].

Therefore, the aim of this work is to obtain new pyridazines containing 1,3,5-triazine moiety by Diels-Alder reaction, to explore reaction mechanism and products structure with computational methods and to investigate possible ways of products modification.

2. Experimental

All the chemicals were purchased from Aldrich Chemical Company (USA) and were used without further purification. 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) for all compounds except diethylamino-derivatives (**5a,b**), for which suitable eluent was not found. The nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were recorded in deuterated chloroform ($CDCl_3$) with Varian VXR (300 MHz) and Varian Mercury (400 MHz) NMR spectrometers, chemical shifts were expressed in δ 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 obtained using hybrid B3LYP [11, 12] functional with 6-31G(d,p) basis set included in the GAUSSIAN 09 Rev.01B [13] program using PCM [14] solvation model ($CHCl_3$). First-order

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saddle points were localized using the standard procedure starting from geometry obtained from PES scan. For optimized structures confirmation of their nature and thermochemical data were obtained using vibrational analysis. Gibbs free energies were used to discuss transition states and products stability. Global reactivity indices of reactants were calculated according to the equations recommended by Parr and Domingo [9, 10] on B3LYP/6-31G(d) level. Atomic Fukui [15, 16] indices were calculated on B3LYP/6-31G(d) level using Jaguar [8] program.

2.1. Diels-Alder Reactions of Azo-bis-Cyanuric Chloride

6,6'-(4,5-dimethylpyridazine-1,2(3H,6H)-diyl)bis (2,4-dichloro-1,3,5-triazine) **(3a).** The solution of 2,3-dimethylbutadiene **(2a)** (0.138 g, 1.69 mmol) was added under stirring to 0.5 g (1.54 mmol) of azo-bis-cyanuric chloride dissolved in 10 ml of chloroform in the presence of dibutylhydroxytoluene (BHT) at 273 K. Within 15 min the deep red solution became colorless and then it was evaporated in vacuum; formed vitreous solid mass was reprecipitated from acetone/hexane and dried under vacuum. Product was obtained with 85% yield as colorless powder not able to crystallize. R_f = 0.73, mp. 431–432 K, ^{1}H NMR (400 MHz, chloroform-*d*) δ, ppm: 4.84 (d, 2H, J = 15.2, CH_2); 3.94 (d, 2H, J = 15.2, CH_2); 1.73 (s, 6H, CH_3); ^{13}C NMR (100 MHz, chloroform-*d*) δ, ppm: 187.9, 187.1, 170.8, 118.7, 55.4 (CH_2), 15.1 (CH_3). LC-MS (*m*/*z*): calc. for [$C_{12}H_{10}Cl_4N_8$ + H^+] 409.07, observed 409.1. Combustion analysis for ($C_{12}H_{10}Cl_4N_8$): Calc. C 35.32, H 2.47, N 27.46, Cl 34.75. Found. C 35.25, H 2.43, N 27.60, Cl 34.67.

Similarly, ***6,6'-(4-methylpyridazine-1,2(3H,6H)-diyl)bis(2,4-dichloro-1,3,5-triazine)*** **(3b)** was obtained: yield 87 %, R_f = 0.74, mp. 434–435 K, ^{1}H NMR (300 MHz, chloroform-*d*) δ, ppm: 5.61 (1 H, br. s.), 5.06 (1 H, d, J = 17.0 Hz), 4.93 (1 H, d, J = 17.1 Hz), 4.09–3.93 (2 H, m), 1.82 (3 H, s.). ^{13}C NMR (75 MHz, chloroform-*d*) δ, ppm: 186.6, 185.7, 170.5, 170.3, 138.5, 121.8 (CH), 50.1 (CH_2), 46.2 (CH_2), 20.5 (CH_3). LC-MS (*m*/*z*): calc. for [$C_{11}H_8Cl_4N_8$ + H^+] 395.05, observed 395.1. Combustion analysis for ($C_{11}H_8Cl_4N_8$): Calc. C 33.53, H 2.05, N 28.44, Cl 35.99. Found. C 33.61, H 2.10, N 28.35, Cl 35.82.

1,2-bis(4,6-dichloro-1,3,5-triazin-2-yl)-1,2,3,6-tetrahydropyridazin-3-yl acetate **(3c).** The solution of 4-acethoxybutadiene **(2c)** (0.189 g, *E/Z* mixture, 1.69 mmol total) in 1 ml of chloroform was added to the solution of 0.5 g (1.54 mmol) of azo-bis-cyanuric chloride in 10 ml of chloroform in the presence of BHT under stirring. The mixture was stirred at 308–313 K for 30 min. The product was isolated from obtained colorless solution as described above. Yield 83 %, colorless powder, R_f = 0.65, mp. 440–442 K. ^{1}H NMR (400 MHz, chloroform-*d*) *d* ppm: 7.46 (1 H, d, J = 2.3 Hz), 6.20 (1 H, dd, J = 10.1, 3.7 Hz), 6.03 (1 H, dt, J = 10.1, 2x2.3 Hz), 5.23 (1 H, dd, J = 18.3, 2.7 Hz), 4.08 (1 H, dd, J = 18.7, 1.4 Hz). ^{13}C NMR (100 MHz, chloroform-*d*) δ, ppm: 172.1, 171.5, 171.3, 170.8, 169.1, 166.33, 165.1, 128.19 (CH), 122.2 (CH), 73.1 (CH), 43.6 (CH_2), 20.4 (CH_3). LC-MS (*m*/*z*): calc. for [$C_{12}H_8Cl_4N_8O_2$ + H^+] 439.06, observed 439.1. Combustion analysis for ($C_{12}H_8Cl_4N_8O_2$): Calc. C 32.90, H 1.84, N 25.58, Cl 32.37, O 7.30. Found. C 33.03, H 1.93, N 25.68, Cl 32.25.

2.2. Obtained Products Modification

6,6'-(4,5-dimethylpyridazine-1,2(3H,6H)-diyl)bis (2,4-dimethoxy-1,3,5-triazine) **(4a)**. 3.7 ml of 3M MeONa solution (8.6 mmol) in methanol were slowly added to the stirred suspension of 1 g (2.46 mmol) of 6,6'-(4,5-dimethylpyridazine-1,2(3H,6H)-diyl)bis(2,4-dichloro-1,3,5-triazine) **(3a)** in 10 ml of methanol. The temperature was maintained at 293–298 K. In 10 min after adding the suspension was diluted with water (50 ml), the precipitate was filtered, washed with water, dried and reprecipitated from acetone/hexane. White powder with 76 % yield was obtained, R_f = 0.79, mp. 459–460 K, ^{1}H NMR (300 MHz, chloroform-*d*) *d* ppm: 4.78 (2 H, d, J = 15.1 Hz), 3.97 (6 H, s), 3.86 (2 H, d, J = 15.1 Hz), 3.83 (6 H, overlapping s), 1.66 (3 H, s). ^{13}C NMR (75 MHz, chloroform-*d*) δ, ppm: 180.0, 179.1, 172.4, 125.6, 56.2 (CH_3), 56.3 (CH_3), 50.0 (CH_2), 16.1 (CH_3).LC-MS (*m*/*z*): calc. for [$C_{16}H_{22}N_8O_4$ + H^+] 391.40, observed 391.4. Combustion analysis for ($C_{16}H_{22}N_8O_4$): Calc. C 49.22, H 5.68, N 28.70, O 16.39. Found. C 49.30, H 5.57, N 28.59.

Similarly, ***6,6'-(4-methylpyridazine-1,2(3H,6H)-diyl)bis(2,4-dimetoxy-1,3,5-triazine)*** **(4b)** was obtained. R_f = 0.77, mp. 455–457 K, ^{1}H NMR (300 MHz, chloroform-*d*) *d* ppm: 5.58 (1 H, br. s.), 4.98 (1 H, d, J=16.9 Hz), 4.90 (1 H, d, J = 17.0 Hz), 3.98–4.15 (14 H, m), 1.82 (3 H, s.). ^{13}C NMR (75 MHz, chloroform-*d*) δ, ppm: 181.0, 180.2, 172.5, 172.3, 138.8, 122.3 (CH), 49.0 (CH_2), 44.9 (CH_2), 20.6 (CH_3).LC-MS (*m*/*z*): calc. for [$C_{15}H_{20}N_8O_2$ + H^+] 377.37, observed 377.4. Combustion analysis for ($C_{15}H_{20}N_8O_2$): Calc. C 47.87, H 5.36, N 29.77, O 17.00. Found. C 47.96, H 5.31, N 29.82.

6,6'-(4,5-dimethylpyridazine-1,2(3H,6H)-diyl)bis (N^2,N^2,N^4,N^4-tetraethyl-1,3,5-triazine-2,4-diamine) **(5a).** Diethylamine (0.448 g, 7.7mmol) and triethylamine (0.620 g, 7.7 mmol) were added to 0.5 g (1.54 mmol) of 6,6'-(4,5-dimethylpyridazine-1,2(3H,6H)-diyl)bis(2,4-dichloro-1,3,5-triazine) (**3a**) dissolved in 10 ml of toluene. The solution was stirred and heated at 353–363 K for 2 h, then cooled, washed with water (3x5 ml), dried with sodium sulfate and vacuum-evaporated. Slight-yellow oil

that slowly hardened was obtained with the yield of 79 %, mp. (–), ^{1}H NMR (400 MHz, chloroform-*d*) *d*, ppm: 4.63 (2 H, d, *J* = 14.6 Hz), 3.80 (2 H, d, *J* = 14.6 Hz), 3.52 (16 H, br. q, *J* = 16.1, 6.9 Hz), 1.64 (6 H, s.), 1.15 (24 H, br.s). LC-MS (*m*/*z*): calc. for [$C_{28}H_{50}N_{12}$ + H^+] 555.78, observed 555.8. Combustion analysis for ($C_{28}H_{50}N_{12}$): Calc. C 60.62, H 9.08, N 30.30. Found C 60.72, H 9.16, N 30.21.

Similarly, ***6,6'-(4-methylpyridazine-1,2(3H,6H)-diyl)bis(N^2,N^2,N^4,N^4-tetraethyl-1,3,5-triazine-2,4-diamine)*** **(5b)** was obtained. mp. (–), ^{1}H NMR (400 MHz, chloroform-*d*) *d*, ppm: 5.59 (1 H, br. s), 5.02 (1 H, d, *J* = 17.2 Hz), 4.91 (1 H, d, *J* = 17.1 Hz), 4.03–3.87 (2 H, m), 3.58 (16 H, br. q, *J* = 15.9, 6.9 Hz), 1.79 (3 H, s.), 1.14 (24 H, br.s). LC-MS (*m*/*z*): calc. for [$C_{27}H_{48}N_{12}$ + H^+] 541.75, observed 541.8. Combustion analysis for ($C_{27}H_{48}N_{12}$): Calc. C 59.97, H 8.95, N 31.08. Found. C 60.09, H 9.03, N 30.97.

3. Results and Discussion

3.1. DFT Calculations

The first part of our work was reactions analysis using global and local reactivity indices, calculated in terms of the one-electron energies of the frontier molecular orbitals, mainly global electrophilicity ω and ΔN_{max} calculated from electronic chemical potential μ and chemical hardness η determined in terms of one electron energies of the frontier molecular orbitals HOMO and LUMO [9, 10]. Azo-bis-cyanuric chloride **(1)** high activity is explained by azo-bond strong electrophilic nature due to electron-withdrawing properties of dichlorotriazine substituents. Its global electrophilicity ω = 4.45 eV makes it one of the most active dienophiles in normal electron demand Diels-Alder reaction, much more active as diethyl azodicarboxylate (DEAD) (2.57 eV) and even more than some Lewis acid complexes, *i.e.* nitroetylene/BH_3 complex (4.33 eV, [17]). Therefore, comparing global electrophylicity indices of reagents, shown in Table 1 polar or zwitterionic mechanism of this cycloaddition could be suggested. Also, reagents local reactivity indices – condensed-to-atoms Fukui functions shown in Table 2 were determined.

In this regard, it was decided to perform transition state search and intrinsic reaction coordinate scan. Expectedly large TS asymmetry, even in case of symmetry of both reagents (azo-cyanuric chloride **(1)** and 2,3-dimethylbutadiene **(2a)**) was found. Calculated TS distances and activation and reaction Gibbs free energies are shown in Table 3. Nevertheless, in all cases no intermediates were found on IRC paths, so this cycloaddition may be classified as two-stage one-step Diels-Alder reaction with highly polar transition state. Reaction mechanism is shown in Scheme 1.

As it could be seen from Tables 1 and 3 transition state asymmetry increases and activation barrier decreases with increasing of reagents electrophilicity differences – from 1-acethoxybutadiene **(2c)** to dimethylbutadiene **(2a)**. It is fully confirmed experimentally as reaction speed increases with growth of the reagents global electrophilicity difference ($\Delta\omega$).

In case of 2-methylbutadiene **(2b)** and 1-acethoxybutadiene **(2c)** TS asymmetry was found to be regioselective, which is confirmed by reagents local reactivity indices – condensed-to-atom Fukui functions for HOMO and LUMO, shown in Table 2. For dienes, which in this reaction are nucleophiles, high values of f^-_{Ak} indicate the most reactive sites for azo-bis-cyanuric chloride **(1)** electrophilic attack – C_4 position of 2-methylbutadiene and C_4 position of 1-acethoxybutadiene. In case of 1-acethoxybutadiene two transition states were located, as it was used as a (*Z*/*E*) mixture of isomers. Activation energy for *(E)*-isomer is about 14.6 kJ/mol lower than for (*Z)* so in kinetically controlled reaction conditions it should be selectively exhausted. But products conformation analysis showed that reaction with (*Z)*-acethoxybutadiene leads to high-lying conformer of (*E)*-product, which cannot be isolated as individual compound. Its instability causes its transformation in reaction conditions to low-lying stage. It is fully confirmed experimentally – in thermodynamically controlled reaction when both isomers were exhausted only one compound was isolated.

Table 1

Reagents global reactivity indices

Molecule (diene or dienophile)	μ, eV	η, eV	ω, eV	ΔN_{max}
Azo-bis-cyanuric chloride **(1)**	-5.91	3.92	4.45	1.51
2,3-Dimethylbutadiene **(2a)**	-3.13	6.03	0.81	0.52
2-Methylbutadiene **(2b)**	-3.32	5.74	0.96	0.58
1-Acethoxybutadiene **(2c)**	-3.49	5.13	1.18	0.68

Table 2

Condensed-to-atoms Fukui functions of reacting compounds

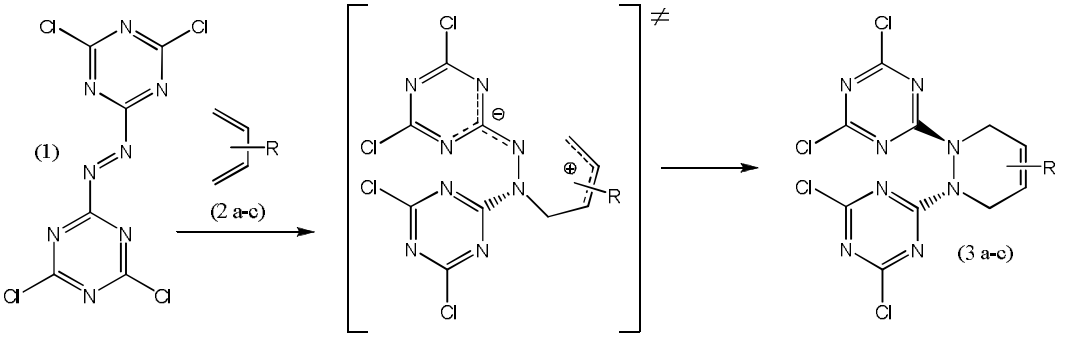
Molecule (diene or dienophile)	Atom	f^-_{Ak}	f^+_{Ak}
Azo-bis-cyanuric chloride **(1)**	N_1/N_2	0.39	**0.26**
2,3-Dimethylbutadiene **(2a)**	C_1/C_4	**0.32**	0.29
2-Methylbutadiene **(2b)**	C_1	**0.38**	0.33
	C_4	**0.27**	0.29
1-Acethoxybutadiene **(2c)**	C_1	**0.25**	0.24
	C_4	**0.29**	0.22

Table 3

Transition state atomic distances and reactions thermodynamic parameters

Diene	$N_1 - C_1$	$N_2 - C_4$	$\Delta G^{\neq}$	ΔG_{rxn}
2,3-Dimethylbutadiene **(2a)**	2.15	2.83	14.3	-44.2
2-Methylbutadiene**(2b)**	2.13	2.75	16.4	-40.7
(*E*)-1-acethoxybutadiene **(2c)**	2.65	2.20	21.0	-33.8
(*Z*)-1-acethoxybutadiene **(2c)**	2.58	2.24	24.5	-21.2*

Note: unstable conformer, relaxes to the same structure as *(E)*-, discussed below.



Scheme 1. DFT-predicted mechanism of cycloaddition

3.2. Synthesis and Further Modification of DA Products

In original article benzene was used as a solvent for DA reactions of azo-bis-cyanuric chloride **(1)**. Products were obtained with moderate yield, *i.e.* 51 % for butadiene, the exception was 86 % for rigidly fixed in *cys*-position cyclopentadiene. Based on reaction mechanism it was proposed that reaction speed and yield should be higher in polar solvents stabilizing highly polar transition state. Azo-bis-cyanuric chloride **(1)** high reactivity makes usage of most polar solvents impossible. We studied its stability and DA reaction time in a large variety of solvents and despite the fact that **(1)** is able to decompose in chloroform for 24 h this solvent was found the most suitable as DA reaction speed is several orders higher than decomposition. The presence of radical reactions inhibitor was found to be essential. Analogous product with butadiene was obtained at 273 K in chloroform in the presence of butylhydroxytoluene (BHT) as polymerization inhibitor in 15 min with 83% yield. Thereby products with 2,3-dimethylbutadiene **(2a)** and 2-methylbutadiene **(2b)** were obtained, the reaction is shown in Scheme 2.

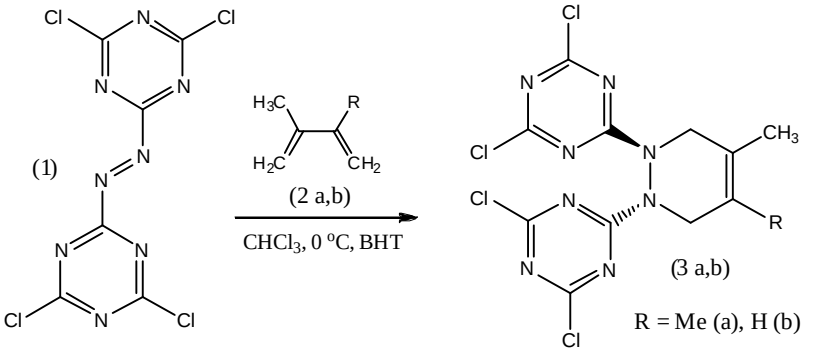
Reaction with 1-acethoxybutadiene **(2c)** was conducted under thermodynamic control conditions at 308–313 K as both isomers were to be exhausted. Reaction mechanism is shown in Scheme 3.

Ways of further products modification by chlorine nucleophilic substitution were also studied. The first attempt was to conduct acid-catalyzed solvolysis in alcohol solution, which for cyanuric chloride is known to pass easily at room temperature. But it was found that product **(3a)** is completely decomposing in methanol for 12 h forming 2-amino-4,6-dimethoxy-1,3,5-triazine as main product. Further research showed that skeleton of all these products is very unstable under acid conditions, but is resistant to strong alkali medium, so all chlorine atoms can be substituted by alkoxy groups by the influence of different sodium alcoholates in suitable solvent, *i.e.* in MeOH or THF at room temperature. This way exhaustively methoxylated derivatives **(4a,b)** were

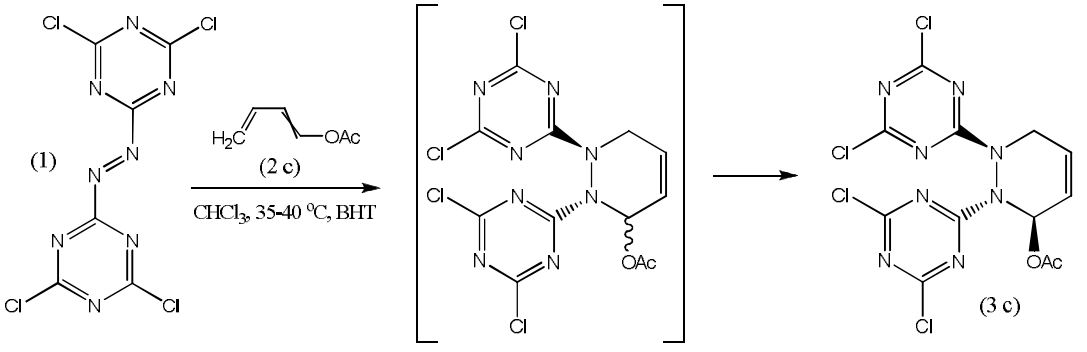
obtained. On the other hand compounds **(3a,b)** were found to be sufficiently thermally stable for amination – no decomposition was observed in boiling toluene for 3 h, which is enough for exhaustively chlorine substitution by different amines. Thereby tetra-diethylamino derivatives were obtained – compounds **(5a,b)**. Investigated ways of products modification are shown in Scheme 4. Compound **(3c)** under analogous conditions formed the mixture of products which were not isolated.

3.3. NMR Characterization and Conformational Analysis of Obtained Products

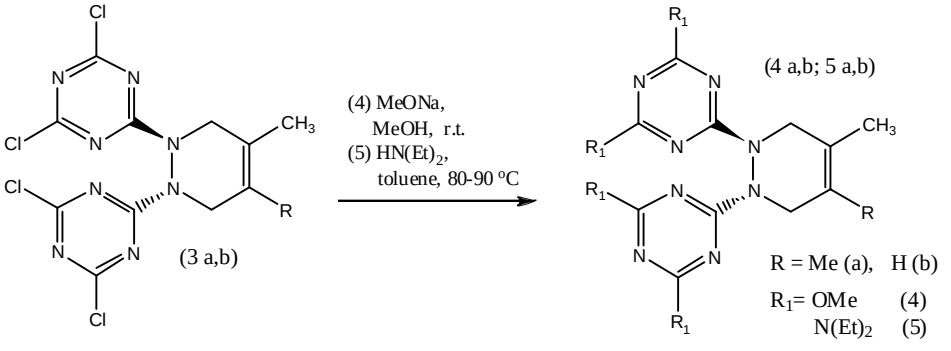
In ^{13}C spectra of all obtained products and in ^{1}H spectra of their methoxylated derivatives signs of 1,3,5-triazine cycles hampered rotation is observed, *i.e.* in ^{1}H NMR of exhaustingly methoxylated 2,3-dimethylbutadiene product **(4a)** methoxy-groups can be seen as two singlets 6H with $\Delta\delta$ = 0.14 ppm. It is caused by 1,3,5-triazine ring magnetic anisotropy – two methoxy-groups are located behind the nearby cycle, other two – on the periphery. A similar splitting with $\Delta\delta$ about 0.8 ppm is observed in ^{13}C NMR spectra. Relaxed coordinate scan showed 104.6–112.9 kJ/mol triazine cycles rotation barrier and over 167.4 kJ/mol barrier of their twisting transition. Hence, it can be concluded that on the one hand this derivatives can form atropisomers with delayed interconversion (in case of different substituents in triazine ring) and on the other hand their stabile spiral chirality due to high barrier of R–S twisting transition of triazine rings.



Scheme 2. Azotriazine reaction with 2,3-dimethylbutadiene and 2-methylbutadiene



Scheme 3. Reaction of azotriazine with (*Z/E*)-1-acethoxybutadiene



Scheme 4. Ways of obtained products modification

4. Conclusions

Diels-Alder reaction between azo-bis-cyanuric chloride and a number of dienes – 2,3-dimethylbutadiene, 2-methylbutadiene and 1-acethoxybutadiene have been carried out and theoretically studied. DFT calculations at the B3LYP/6-31G(d,p) level showed that cycloaddition may be classified as asynchronic concert Diels-Alder reaction. High transition state polarity is consistent with major influence of solvent polarity on reaction speed, so relatively inert polar solvents, such as chloroform and acetonitrile are the most suitable for this reaction. Products were found to be stable both thermally and in alkaline conditions hereby opening the way to their further modification by chlorine atoms substitution. Conformation analysis of products showed large barrier of 1,3,5-triazine rings rotation and twisting translation, which provides stability of their optical isomers and possibility of atropisomers formation.

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ЕКСПЕРИМЕНТАЛЬНІ ТА DFT-ДОСЛІДЖЕННЯ ПОЛЯРНОЇ РЕАКЦІЇ ДІЛЬСА-АЛЬДЕРА АЗО-БІС-ЦІАНУРХЛОРИДУ З РЯДОМ ДІЄНІВ. ШЛЯХИ ПОДАЛЬШОЇ МОДИФІКАЦІЇ ОДЕРЖАНИХ ПРОДУКТІВ

Анотація. *Була проведена та досліджена на B3LYP/6-31G(d,p) рівні реакція Дільса-Альдера азо-біс-ціанурхлориду як електрофільного дієнофілу з рядом дієнів з різною нуклеофільністю, а саме 2,3-диметилбутадієну, 2-метилбутадієну і 1-ацетоксибутадієну. Визначено, що реакція проходить за м'яких умов та з високими виходами. Обчислені глобальні та локальні індекси реакційності, а також геометрії перехідних станів та енергії активації. Вивчені напрямки подальшої модифікації одержаних продуктів заміщенням атомів хлору. Встановлено, що сполуки є стійкими в лужних умовах, але швидко руйнуються у присутності кислот.*

Ключові слова: *реакція Дільса-Альдера, DFT розрахунки, 1,3,5-триазин, конформаційний аналіз.*