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Participation of Phosphorylated Analogues of Nitroethene in Diels–Alder Reactions with Anthracene: A Molecular Electron Density Theory Study and Mechanistic Aspect

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Abstract: The structure and the contribution of the bis(2-chloroethyl) 2-nitro **1a** and 2-bromo-2-nitroethenylphosphonates **1b** with anthracene **2** in the Diels–Alder (DA) reactions have been studied within the Molecular Electron Density Theory (MEDT) at the B3LYP functional together with 6-31G(d), 6-31+G(d) and 6-31+G(d,p) basic sets. Analysis of the Conceptual Density Functional Theory (CDFT) reactivity indices indicates that **1a** and **1b** can be classified as a strong electrophile and marginal nucleophile, while **2** is classified as a strong electrophile and strong nucleophile. The studied DA reactions take place through a one-step mechanism. A Bonding Evolution Theory (BET) of the one path associated with the DA reaction of **1a** with **2** indicates that it is associated with non-concerted *two-stage one-step* mechanism. BET analysis shows that the first C2-C3 single bond is formed in *Phase VI*, while the second C1-C6 single bond is formed in the *Phase VIII*. The formation of both single bonds occurs through the merging of two C2 and C3, C1 and C6 *pseudoradical* centers, respectively.

Keywords: Diels–Alder reaction; anthracene; molecular mechanism; bonding evolution theory; molecular electron density theory

1. Introduction

The Diels–Alder (DA) reaction is among the most formidable available protocols for the construction of optically active compounds, with extensive synthetic applications in natural products with a large range of biological activity [1–4]. Many studies concerning of the DA reactions put these reactions in a completely different light; a one-step mechanism has been replaced by a two-step mechanism undergoing through the intermediate. *Korotayev* and *Sosnovsky* [5] presented experimental studies of the reaction between (E)-1,1,1-trifluoro-3-nitrobut-2-ene and 3,3-dimethyl-2-morpholinbutene (Scheme 1) in which, apart from the main product, the Authors confirmed the presence of an acyclic adduct. Recently theoretical studies [6] confirm the stepwise, zwitterionic mechanism formation of final, internal nitronate.

In 2011, *Korotaev* and co-workers [7] studied the reactions of α -(trihaloethylidene)-nitroalkanes with push–pull enamines (Scheme 2). It was found that the reaction of α -(trihaloethylidene)-nitroalkanes with push–pull enamines affords one to cycloadduct or linear enamines depending on the nature of the trihalomethyl group.

In the case of the experimental [8] and theoretical [9] research of the reaction between 1-methylpyrrole and dimethyl acetylenedicarboxylate two alternative reaction pathways have also been considered. This reaction proceeds with a two-step formation of cycloadduct, and intramolecular proton transfer affords a Michael adduct (Scheme 3).





Scheme 1. Experimentally and theoretically observed course of reaction between (E)-1,1,1-trifluoro-3-nitrobut-2-ene and 3,3-dimethyl-2-morpholinobutene [5,6].



Scheme 2. Experimentally observed course of reaction between α -(trihaloethylidene)-nitroalkanes with push-pull enamines [7].



Scheme 3. Experimentally and theoretically observed course of reaction between 1-methylpyrrole with dimethyl acetylenedicarboxylate [8,9].

Anisimova and co-workers [10], examined the reactions of the bis(2-chloroethyl) 2-nitro **1a** and 2-bromo-2-nitroethenylphosphonates **1b** with anthracene **2** which lead to product **3a**,**b** and trace amounts of acyclic adduct **4a**,**b** (Scheme 4). The authors did not undertake any research on the mechanism of these reactions. Based on the presence of an acyclic product **4a**-**b** in the post-reaction mixture, we can suspect the formation of **3a**-**b** to come about by a two-step mechanism. In this case, the possibility of creating a product **3a**-**b** through a two-step mechanism is highly presumable. On this basis, the mechanism of the bis(2-chloroethyl) 2-nitro **1a** and 2-bromo-2-nitroethenylphosphonates **1b** with anthracene **2** require a deeper exploration. To fill the gap that has arisen, we seal to execute the Molecular Electron Density Theory (MEDT) [11] analysis, in which a connection of the analysis of

reaction profiles, key stationary structures and the Bonding Evolution Theory (BET) [12] analysis of the molecular mechanism of reaction bis(2-chloroethyl)-2-nitroethenylphosphonates **1a** with anthracene **2**.



Scheme 4. Experimentally observed course of the reaction bis(2-chloroethyl) 2-nitro 1a and 2-bromo-2-nitroethenylphosphonates **1a**,**b** with anthracene **2** [10].

2. Computational Details

All calculations associated with the DA reactions were performed using the GAUSSIAN 16 package [13] in the Prometheus computer cluster of the CYFRONET regional computer center in Cracow. The geometries of all reactants, transition state structures (TSs) and products of the reactions were fully optimized using the B3LYP [14] functional together with the 6-31G(d), 6-31+G(d) and 6-31+G(d,p) basis sets. This computational level has already been successfully used for the exploration of a reaction involving several different nitrocompounds and others [15–19]. Intrinsic reaction coordinate (IRC) calculations [20] were achieved in all instances to verify that the located TSs are connected to the corresponding minimum stationary points associated with reactants and products. The solvent effects of benzene were simulated using a relatively simple self-consistent reaction field (SCRF) [21–23] based on the polarizable continuum model (PCM) of Tomasi's group [24,25]. The values of energies, enthalpies, entropies and Gibbs free energies were calculated for temperature 353K. The global electron density transfer (GEDT) [26] values were calculated as the sum of the natural atomic charges (q), obtained by a Natural Population Analysis (NPA) [27,28], by the equation: GEDT (f) = $\sum_{i=1}^{n} q$ for all atoms belonging to each fragment (f) of the TSs at the B3LYP(PCM)/6-31G(d) level q∈f of theory.

Indexes of σ -bonds development (l) were designed according to equation [15]:

$$l_{X-Y} = 1 - \frac{r_{X-Y}^{TS} - r_{X-Y}^{P}}{r_{X-Y}^{P}}$$

where r^{TS}_{X-Y} is the distance between the reaction centers X and Y in the transition structure and r^{P}_{X-Y} is the same distance in the corresponding product.

Global electronic properties of the reactants were estimated according to the equations recommended in references [29,30]. The electronic chemical potentials (μ), chemical hardness (η) and global nucleophilicity (N) have been calculated according to a well-known protocol [31,32]. Electrophilic P_k^+ and nucleophilic P_k^- . Parr functions [33] were obtained from the changes of atomic spin density (ASD) of the reagents.

Electron Localization Function (ELF) [34] research was accomplished with the TopMod package [35]. The bonding modifications through the analyzed reaction were studied, according to the BET [12], by executing the topological analysis of the ELF for 173 nuclear configurations along the IRC path. The ELF molecular geometries and basin attractor positions were depicted using the GaussView program [36]. ELF localization domains were represented by using the Paraview software at an

isovalue of 0.75 a.u [37,38]. A similar approach has been successfully used to explain the mechanism of different types of reactions [16–19,39].

3. Results and Discussion

The present theoretical study has been divided into three parts: (i) first, the analysis of the conceptual density functional theory (CDFT) reactivity indices and ELF characterization of the reactants was carried out (ii) second, the DA reaction profiles of the bis(2-chloroethyl) 2-nitro- **1a** and bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonates **1b** with anthracene **2** including full diagnostic of all critical structures are explored and characterized (iii) and next, a BET study of the reaction between bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a** and anthracene **2**, in order to characterize the molecular mechanism was performed.

3.1. Analysis of the CDFT Reactivity Indices and ELF Characterization of the Reactants

In order to understand the contribution of reagents in the DA reactions, the analysis of the global indices was achieved at the B3LYP/6-31G(d) level of theory, within the context of the CDFT [29,30]. The electronic chemical potential μ , chemical hardness η , global electrophilicity ω and global nucleophilicity N are collected in Table 1.

Table 1. B3LYP/6-31G(d) electronic chemical potential μ , chemical hardness η , global electrophilicity ω , and global nucleophilicity N, in eV, for the studied reagents.

	μ	η	ω	Ν
1a	-5.59	5.19	3.01	0.94
1b	-5.62	4.74	3.33	1.13
2	-3.43	3.59	1.64	3.89

The electronic chemical potential [40] μ of 2, -3.34 eV, is higher than that of 1a and 1b, -5.59 eV and -5.62 eV, respectively. On the basic of the calculated values of the electronic chemical potential, it can be concluded that the GEDT [27,28] in these DA reactions will proceed from anthracene 2 towards to bis(2-chloroethyl) 2-nitro nitroethenylphosphonate 1a and bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonates 1b. The electrophilicity [31] ω and global nucleophilicity [32] N indices of 1a are 3.01 eV and 0.94 eV and for 1b are 3.33 eV and 1.13 eV. Based on the electrophilicity [41] and nucleophilicity [42] scale, 1a and 1b can be classified as a strong electrophile and marginal nucleophile. In turn, the electrophilicity ω and global nucleophilicity N indices of 2 are 1.64 eV and 3.89 eV, respectively. According to that, 2 can be classified as a strong electrophile but remaining a strong nucleophile.

The electron density changes on the electrophile and nucleophile can be sensed by the nucleophilic P_k^- . and electrophilic P_k^+ Parr functions [33], which are good predictors for local reactivity in polar processes. The electrophilic P_k^+ and the nucleophilic P_k^- . and Parr functions for the GS of the reagents are gathered in Figure 1.

An analysis of the electrophilic P_k^+ Parr functions of **1a**, $P_k^+ = 0.33$ and **1b**, $P_k^+ = 0.31$, indicates that C2 atoms in both are the most electrophilic their center. In turn, the C1 atoms in **1a**, $P_k^+ = 0.15$ and **1b**, $P_k^+ = 0.16$, indicate the lower electrophilic character. In the case of **2**, an analysis of the nucleophilic P_k^- Parr functions, indicate that C3, $P_k^- = 0.29$, and C6, $P_k^- = 0.29$, are the most nucleophilic center in the molecule while C4, C5, C7 and C8 centers show negligible nucleophilic characters.

In order to characterize the ELF structures of bis(2-chloroethyl) 2-nitro- **1a** and bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonates **1b** with anthracene **2** a quantum chemical analysis of Becke and Edgecombe's ELF [34] was conducted. Figure 2 shows the most important valence basin populations and ELF localization domains.



Figure 1. 3D representations of the ASD of the radical anion $1a^{-}$ and $1b^{-}$ and the radical cation $2a^{+}$, together with the electrophilic P_k^+ Parr functions of 1a-b and the nucleophilic P_k^- Parr functions of 2.



Figure 2. B3LYP/6-31G(d) basin attractor positions together with the most significant valence basin populations of bis(2-chloroethyl) 2-nitronitroethenyl-phosphonate **1a** and bis(2-chloroethyl) 2-bromo-2-nitroethenyl-phosphonate **1b** with anthracene **2**.

ELF topological analysis of bis(2-chloroethyl) 2-nitroethenylphosphonate **1a**, in the most important region, shows the presence of two V(C1,C2) and V'(C1,C2) disynaptic basins integrating the same value of 1.74 e. In the bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonate **1b**, we also find, in the most important region, V(C1,C2) and V'(C1,C2) disynaptic basins integrating 1.85 e and 1.84 e, respectively. These disynaptic basins are associated with C1-C2 double bonds in **1a** and **1b** molecules. In turn, an ELF topological analysis of anthracene **2** of the C-C bonding regions belonging to the aromatic rings are characterized by the presence of six V(C3,C4), V(C4,C5), V(C5,C6), V(C6,C7), V(C7,C8) and V(C8,C3) disynaptic basins integrating in all cases 2.47 e–2.93 e (Figure 2). These disynaptic basins are connected with partial double bonds in the most important region in anthracene **2**.

3.2. DA Reaction Profiles of the bis(2-chloroethyl) 2-nitro- 1a and bis(2-chloroethyl) 2-bromo-2-Nitroethenylphosphonates 1b with Anthracene 2

Second, the DA reactions between bis(2-chloroethyl) 2-nitro- **1a** and bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonates **1b** with anthracene **2** were studied. The relative electronic energies of the stationary points involved in the DA reactions between **1a-b** and **2** are presented in Scheme **5**. A one-step mechanism is determined for these DA reactions after to perform a carefully of the corresponding stationary points (Scheme **5**).



Scheme 5. DA reaction of the bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a** and bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonates **1b** with anthracene **2**. B3LYP(PCM)/6-31G(d) relative energies are given in kcal·mol⁻¹.

The quantum-chemical calculations show that the reactions **1a-b** with **2** in the benzene solution at the initial stage lead to molecular complexes (MCs). The energy is reduced until the formation of MCs located 1.6 (**MC1**) and 3.0 (**MC2**) kcal/mol bellow the separated reagents takes place. The activation energy associated with the reactions **1a-b** with **2**, via **TS1** and **TS2**, presents a high value, 22.4 kcal·mol⁻¹ and 19.3 kcal·mol⁻¹, respectively. Then, formation of the final products **3a-b** are exothermic by 13.0 kcal·mol⁻¹ and 14.4 kcal·mol⁻¹, respectively. The relative enthalpies, Gibbs free energy and entropies of the stationary points involved in the DA reactions between 2-nitro-ethenylphosphonate **1a**, bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonates **1b** and anthracene **2** are given in Table 2. B3LYP(PCM)/6-31G(d) the activation Gibbs free energy associated with DA reactions **1a-b** and **2**, via **TS1** and **TS2** is 36.8 kcal·mol⁻¹ and 35.2 kcal·mol⁻¹, respectively. The calculations carried out using 6-31+G(d) and 6-31+G(d,p) basic sets (see Table S1 in Supplementary Information) show increase of Gibbs free energy in the case of reaction between bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a** and anthracene **2**, for **TS1** 38.5 kcal·mol⁻¹ and 38.8 kcal·mol⁻¹, respectively. In turn, in the case of the reaction between bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonates **1b** and anthracene **2**, we observed the reduction of Gibbs free energy for **TS2**, 30.3 kcal·mol⁻¹ and 31.2 kcal·mol⁻¹, respectively.

Table 2. B3LYP(PCM)/6-31G(d) The relative enthalpies, Gibbs free energy (Δ H and Δ G, in kcal·mol⁻¹) and entropies (Δ S, in cal·mol⁻¹·K⁻¹), computed in benzene, for the stationary points involved in the reactions of the bis(2-chloroethyl) 2-nitro **1a** and bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonates **1b** with anthracene **2**.

Transition	ΔH_{353}	ΔG_{353}	ΔS_{353}
1+2→MC1	-2.1	7.9	-33.7
1+2→TS1	21.8	36.8	-50.4
1+2→3a	-13.6	1.5	-50.7
1+2→MC2	-3.6	4.8	-28.0
1+2→TS2	18.7	35.2	-55.3
1+2→3b	-15.0	3.8	-63.0

Optimized critical structures for the DA reactions between **1a-b** and **2**, including some selected distances and key parameters, are given in Figure 3 and Table 3. At **TS1**, the distance between the C1 and C6, and the C2 and C3 interacting atoms are 2.106 Å, and 2.430 Å, respectively. These values suggest an asynchronous bond formation process. We also observe the same relationship in the case of **TS2** in DA reaction of the bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonate **1b** with anthracene **2** (Figure 3, Table 3). The DA reactions of **1a-b** and **2** were analyzed by computing the GEDT [26] (Table 3). The GEDT, for the transition states of the reaction **1a-b** with **2**, are for **TS1** 0.30 e and for **TS2** 0.36 e. Based on the calculated GEDT values, we can conclude that these reactions show strong polar character of DA reactions between **1a-b** and anthracene **2**.



Figure 3. Views of critical structures for DA reaction of bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a** and bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonates **1b** with anthracene **2** in the light of B3LYP(PCM)/6-31G(d) calculations.

Structure -	C2-C3		C1-C6			GEDT	Imaginary	
	r [Å]	1	r [Å]	1	ΔΙ	[e]	Frequency [cm ⁻¹]	
MC1 TS1 3a	6.816 2.106 1.576	0.664	3.925 2.430 1.566	0.448	0.22	0.30	-399.48	
MC2 TS2 3b	7.256 1.958 1.581	0.762	5.187 2.805 1.561	0.203	0.56	0.36	-332.75	

Table 3. Key parameters of critical structures for DA reactions of bis(2-chloroethyl) 2-nitro and 2-bromo-2-nitroethenylphosphonates **1a,b** and anthracene **2** according to B3LYP(PCM)/6-31G(d) calculations.

3.3. BET Study of the DA Reaction between bis(2-chloroethyl) 2-nitro-ethenylphosphonate 1a and Anthracene 2

A BET study of the analyzed reaction of the bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a** and anthracene **2** was carried out, in order to understand the bonding changes in this reaction. Scheme 6 contains the molecular mechanism depicted by Lewis-like structures resulted from the ELF topology. In turn, the populations of the most important valence basins are assembled in Table 4.

The DA reaction of bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a** with anthracene **2** takes place along eight different phases. *Phase* I, 3.49 Å \geq d(C2-C3) > 2.66 Å and 3.64 Å \geq d(C1-C6) > 2.43 Å, begins at molecular complex (**MC1**), which corresponds with the first structure of the IRC path. The ELF picture of **MC1** is practically the same as the ELF picture of the separated reagents (Table 4).

Phase II begins at **P1**, 2.66 Å \geq d(C2-C3) > 2.50 Å and 2.43 Å \geq d(C1-C6) > 2.21 Å. At this point, we observed the merger of the two V(C1,C2) and V'(C1,C2) disynaptic basins, present in the previous point, into one new V(C1,C2) disynaptic basin, integrating 3.32 e. This topological change is connected with a rupture of the double C1-C2 in bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a**.

Phase III, 2.50 Å \geq d(C2-C3) > 2.45 Å and 2.21 Å \geq d(C1-C6) > 2.13 Å, starts at **P2**, with energy cost of 17.1 kcal·mol⁻¹. The ELF picture of **P2**, shows the presence of a new V(C3) monosynaptic basin, integrating 0.13 e (Figure 4). This topological change is related to the formation of a new *pseudoradical* center at C3 carbon in effect of depopulation V(C8,C3) and V(C3,C4) disynaptic basins.



Scheme 6. Simplified representation of the molecular mechanism of the DA reaction between bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a** and anthracene **2** by Lewis-like structures ensuing from the Electron Localization Function (ELF) analysis lengthwise the reaction path.

Table 4. ELF valence basin populations, distances of the forming bonds, B3LYP(PCM)/6-31G(d) relative electronic energies ^a, **MC1–3a**, defining the eight phases characterizing the molecular mechanism of the DA reaction between bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a** and anthracene **2. MC1**, **TS1** and the cycloadduct **3a** are also caught. Distances are given in angstroms, Å, electron populations in average number of electrons, e, relative energies in kcal·mol⁻¹.

Points	1a	2	MC1	P1	P2	P3	P4	P5	P6	P 7	3a	TS1
Phase	Phases I		Ι	II	III	IV	V	VI	VII	VIII		
d(C2-C3))		3.489	2.659	2.502	2.449	2.412	2.356	2.316	2.184	1.566	2.430
d(C1-C6))		3.643	2.429	2.208	2.132	2.081	2.005	1.956	1.821	1.576	2.106
ΔΕ			0.0	8.5	17.1	22.0	21.8	15.8	5.5	-2.7	-11.5	24.0
V(C1,C2)) 1.74		1.75	3.32	3.19	2.95	2.69	2.55	2.45	2.22	1.99	2.87
V′(C1,C2	2)1.74		1.69									
V(C3,C4))	2.71	2.81	2.65	2.58	2.55	2.53	2.49	2.45	2.33	2.05	2.54
V(C4,C5))	2.47	2.45	2.59	2.60	2.61	2.62	2.65	2.66	2.70	2.75	2.61
V(C5,C6))	2.71	2.79	2.65	2.50	2.40	2.35	2.29	2.23	2.16	2.05	2.37
V(C6,C7))	2.93	2.83	2.69	2.53	2.46	2.41	2.34	2.31	2.22	2.07	2.44
V(C7,C8))	2.47	2.48	2.54	2.60	2.61	2.62	2.64	2.65	2.69	2.77	2.61
V(C8,C3))	2.93	2.81	2.76	2.69	2.64	2.61	2.61	2.47	2.33	2.06	2.61
V(C3)					0.13	0.23	0.32					0.28
V(C2)						0.34	0.45					0.40
V(C1)							0.38	0.50	0.57			
V(C2,C3))							0.96	1.07	1.38	1.76	
V(C6)									0.15			
V(C1,C6))									1.02	1.79	

^a Relative to the first point of the IRC, **MC1**.

Phase IV, 2.45 Å \geq d(C2-C3) > 2.41 Å and 2.13 Å \geq d(C1-C6) > 2.08 Å, begins at **P3**. In this phase, we notice the emergence of a new V(C2) monosynaptic basin integrating 0.34 e. This topological change is connected with formation a second new *pseudoradical* center at C2 carbon atom (Figure 4). Together with this change, the V(C1,C2) disynaptic basin experiences a depopulation to 2.95 e at **P3**. The transition state **TS1** of the HDA reaction is found in this phase, d(C2-C3) = 2.43 Å and d(C2-C6) = 2.10 Å (Table 4).

Phase V, 2.41 Å \geq d(C2-C3) > 2.36 Å and 2.08 Å \geq d(C1-C6) > 2.01 Å, starts at **P4** and is characterized by the creation of a new V(C1) monosynaptic basin, integrating 0.38 e. This topological change is related to the formation of a *pseudoradical* center at the C1 carbon. The electron density for formation of *pseudoradical* center at C1 comes from the C1-C2 bonding region which experiences depopulation from 2.95 e at **P3** to 2.69 e at **P4**.

Phase VI, 2.36 Å \geq d(C2-C3) > 2.32 Å and 2.01 Å \geq d(C1-C6) > 1.96 Å, begins at **P5**. At the beginning of this phase, the first most relevant change along the IRC path takes place. The two V(C2) and V(C3) current at **P4** are missing, a new V(C2,C3) disynaptic basin, integrating 0.96 e, is established. These topological changes are connected with formation of the first C2-C3 single bond. A C2-C3 bond begins to form at a C-C distance of 2.356 Å (Figure 4).

Phase VII, 2.32 Å \geq d(C2-C3) > 2.18 Å and 1.96 Å \geq d(C1-C6) > 1.82 Å, starts at **P6**, which is characterized by formation of a new V(C6) monosynaptic basin, integrating 0.15 e. This topological change is related to formation the next *pseudoradical* center at C6 carbon.

The last *Phase VIII*, 2.18 Å \geq d(C2-C3) > 1.57 Å and 1.82 Å \geq d(C1-C6) > 1.58 Å, is located between points **P7** and final product **3a**. The ELF picture of **P7** feature the formation of a new V(C2,C6) disynaptic basin, integrating 1.02 e, as a result of the merger of the two V(C2) and V(C6) monosynaptic basins. These topological changes are related with formation of a second C2-C6 single bond in **3a** molecule.



Figure 4. The most important ELF valence basins of the structure P2–P7 aligned in the two C-C single bond formation in the reaction between bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a** and anthracene **2**. The electron populations, in average number of electrons, are given in e.

Based on the BET analysis, some appealing conclusions concerning the mechanism of DA reaction of the bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a** and anthracene **2** can be drawn: (i) the mechanism of analyzed DA reaction can be topologically characterized by eight different phases (see Table 4); (ii) at the beginning of the reaction, we observed the rupture of the C1-C2 double bond in bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a**; (iii) next, we observed formation of three pseudoradical centers at C3, C2 and C1 carbon atoms; (iv) the formation of the first C2-C3 single bond occurs at point **P5** (see Figure 4 and Scheme 6); (v) in the next phase we observed the formation of pseudoradical center at C6 carbon and next creation of the second C1-C6 single bond. The formation of both single bonds occurs through the merging of two C2 and C3, C1 and C6 pseudoradical centers, respectively.

4. Conclusions

The reactions of the bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a** and bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonate **1b** with anthracene **2** have been analyzed within the MEDT study at the B3LYP(PCM)/6-31G(d) calculations. The received results are supported by the combination of

the analysis of the CDFT reactivity indices at the ground state of the reagents, analyzed of the reaction profiles and BET study of the one exemplary reaction path.

Analysis of reactivity indices chances are that the strong electrophilic character of the bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a** and bis(2-chloroethyl) 2-bromo-2-nitroethenylphosphonate **1b**. The aforementioned analysis showed that anthracene **2** can be classified as a strong electrophile while remaining a strong nucleophile. ELF analysis of electronic structures of 1a and 1b shows that they have in the most important region, two V(C1,C2) and V'(C1,C2) disynaptic basins. These disynaptic basins are associated with C1-C2 double bonds. An ELF topological analysis of anthracene **2** of the C-C bonding regions belonging to the aromatic rings are characterized by the presence of six disynaptic basins which are connected with partial double bonds.

The present MEDT study established DA reactions between phosphorylated analogues of nitroethene and anthracene. DA reactions of the **1a-b** with **2** should be regarded as a two-stage one-step process. BET analysis of the molecular mechanism associated with the DA reaction of bis(2-chloroethyl) 2-nitro-ethenylphosphonate **1a** with anthracene **2** indicates that it is initialized by the rupture of the C1-C2 double bond in **1a** molecule and formation of three *pseudoradical* centers at C1, C2 and C3 carbon. In the next stage we observed the formation of first C2-C3 single bond, a new *pseudoradical* center at C6 carbon and in the last stage of the reaction and the formation of a second C1-C6 single bond.

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