

Article

Not peer-reviewed version

On the Jahn-Teller Effect in Silver Complexes of Dimethyl Amino Phenyl Substituted Phthalocyanine

[Martin Breza](#) *

Posted Date: 13 September 2023

doi: [10.20944/preprints202309.0815.v1](https://doi.org/10.20944/preprints202309.0815.v1)

Keywords: DFT; TD-DFT; symmetry descent; electron states; vibronic interactions



Preprints.org is a free multidiscipline platform providing preprint service that is dedicated to making early versions of research outputs permanently available and citable. Preprints posted at Preprints.org appear in Web of Science, Crossref, Google Scholar, Scilit, Europe PMC.

Copyright: This is an open access article distributed under the Creative Commons Attribution License which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Disclaimer/Publisher's Note: The statements, opinions, and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions, or products referred to in the content.

Article

On the Jahn-Teller Effect in Silver Complexes of Dimethyl Amino Phenyl Substituted Phthalocyanine [†]

Martin Breza ^{*}

Department of Physical Chemistry, Slovak Technical University, Radlinskeho 9, SK-81237 Bratislava, Slovakia

^{*} Correspondence: martin.breza@stuba.sk

[†] Dedicated to Professor Andrej Staško in honor of his 85th birthday.

Abstract: The structures of Ag complexes with dimethyl amino phenyl substituted phtalocyanine $m[\text{dmaphPcAg}]^q$ of various charges q and in two lowest spin states m were optimized using the B3LYP method within the D_{4h} symmetry group and its subgroups. The most stable reaction intermediate in the supposed photoinitiation reaction is ${}^3[\text{dmaphPcAg}]^1$. Group-theoretical analysis of the optimized structures and of their electron states reveals two symmetry-descent mechanisms. Stable structures of maximal symmetry of complexes ${}^1[\text{dmaphPcAg}]^+$, ${}^3[\text{dmaphPcAg}]^+$, ${}^2[\text{dmaphPcAg}]^0$ and ${}^4[\text{dmaphPcAg}]^2$ correspond to the D_4 group as a consequence of the pseudo-Jahn-Teller effect within unstable D_{4h} structure. Complexes ${}^4[\text{dmaphPcAg}]^0$, ${}^1[\text{dmaphPcAg}]^-$, ${}^3[\text{dmaphPcAg}]^-$ and ${}^2[\text{dmaphPcAg}]^2$ with double degenerate electron ground states in D_{4h} symmetry structures undergo a symmetry descent to stable structures corresponding to maximal D_2 symmetry not because of a simple Jahn-Teller effect but due to hidden pseudo-Jahn-Teller effect (strong vibronic interaction between excited electron states). The reduction of the neutral photoinitiator causes symmetry descent to its anionic intermediate because of vibronic interactions that must significantly affect the polymerization reactions.

Keywords: DFT; TD-DFT; symmetry descent; electron states; vibronic interactions

1. Introduction

New photosensitive systems with improved efficiency for initiating free-radical and/or cationic polymerizations under light activation are developed using sophisticated chemical treatments. Very recently, Breloy et al. [1] synthesized dimethyl amino substituted phtalocyanine dmaphPcH₂ and its Ag(II) complex ${}^2[\text{dmaphPcAg}]^0$ (Figure 1). Photoexcitation of $[\text{dmaphPcAg}]^0$ in the presence and absence of an iodonium salt produced acidic and radical species that initiated cationic and free-radical polymerizations, respectively. The photoinitiator properties were investigated by spectroscopic and quantum-chemical methods. The polymerization kinetics in laminate and under air was studied. In the first step, irradiation (385 and 405 nm) caused a reduction of Ag(II) to Ag(I) and nitrogen-centered radicals were formed. Subsequently, Ag nanoparticles and carbon-centered radicals developed. Intermediates $[\text{dmaphPc}]^1$, Ag^0 nanoparticles, and $[\text{dmaphPcAg}]^q$ complexes, $q = -1 \rightarrow +1$, are supposed within the proposed reaction mechanism. DFT calculations indicate a $D_4 \rightarrow D_2$ symmetry descent in $[\text{dmaphPcAg}]^q$ complexes which could be ascribed to the Jahn-Teller (JT) effect. The aim of our recent study is to shed more light on this problem and to verify the above explanation using a group theoretical analysis of the DFT optimized structures of $[\text{dmaphPcAg}]^q$ complexes within the highest possible D_{4h} symmetry group and its subgroups.

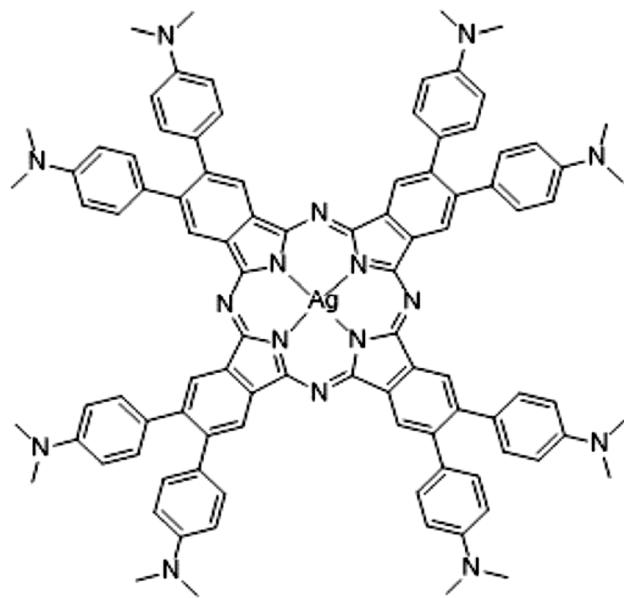


Figure 1. Structure of ${}^2[\text{dmaphPcAg}]^0$ [1].

2. Theoretical background

According to the Jahn-Teller theorem [2], any nonlinear configuration of atomic nuclei in a degenerate electron state is unstable. Hence, there is at least one such configuration of lower symmetry, where the above degeneracy is removed. In other words, the multidimensional representation in the high-symmetric (HS) structure is split into nondegenerate representations in the low-symmetric (LS) structure.

The JT active coordinate Q_{JT} describes the above mentioned symmetry descent. If the potential energy surface $E = f(Q_i)$ of N atoms is a function of $3N - 6$ independent nuclear coordinates Q_i , for the JT 'unstable' HS structure the following relation for any Q_{JT} is valid

$$\left(\frac{\partial E}{\partial Q_{\text{JT}}}\right)_{\text{HS}} \neq 0 \quad (1)$$

The HS \rightarrow LS geometry change described by Q_{JT} is connected with an energy decrease which is denoted as the JT stabilization energy E_{JT}

$$E_{\text{JT}} = E_{\text{HS}} - E_{\text{LS}} \quad (2)$$

An analogous symmetry descent and energy decrease for pseudodegenerate electron states is known as the pseudo-Jahn-Teller (PJT) effect. It can be observed for a sufficiently strong vibronic interaction and relatively small energy difference Δ_{ij} between the interacting electron states Ψ_i and Ψ_j [3].

The (P)JT effects are usually related to the ground state Ψ_0 (and some of the excited states Ψ_j). Nevertheless, excited states can undergo to these effects as well. In some cases the corresponding vibronic interaction can be so strong that the lower surface penetrates the potential surface of the ground electron state corresponding the HS structure and becomes the lowest state in the LS structure (i.e. its ground electron state). These consequences of the strong JT and PJT vibronic interactions within excited electron states are known as the hidden JT (HJT) and hidden PJT (HPJT) effects, respectively [4].

The (P)JT potential surfaces can be described by an analytical function based on perturbation theory. However, the search for their extremal points corresponding to the 'stable' or 'unstable' (P)JT structures is too complicated for large molecular systems. In such cases, a group-theoretical treatment must be used.

The epikernel principle method [5,6] is based on the Q_{JT} symmetry in the HS structure. A nonzero value of the integral

$$\langle \Psi_i \left| \frac{\partial \hat{H}}{\partial Q_{JT}} \right| \Psi_j \rangle \neq 0 \quad (3)$$

for the interacting electron states Ψ_i and Ψ_j and the full-symmetric Hamilton operator \hat{H} demands that the direct product

$$\Gamma_i^* \otimes \Lambda_{JT} \otimes \Gamma_j \quad (4)$$

where Γ_i , Λ_{JT} , and Γ_j are representations of Ψ_i , Q_{JT} , and Ψ_j , respectively (the asterisk denotes a complex conjugate value), must contain a full-symmetric representation. Alternatively

$$\Lambda_{JT} \in \Gamma_i^* \otimes \Gamma_j \quad (5)$$

In the case of the JT effect and the degenerate states $\Psi_i = \Psi_j$, i.e. $\Gamma_i = \Gamma_j$, we obtain the even stronger condition

$$\Lambda_{JT} \in [\Gamma_i \otimes \Gamma_i]^+ \quad (6)$$

where $[...]^+$ denotes the symmetric direct product.

The epikernel principle states that the extrema of a JT energy surface correspond to the kernel $K(G, \Lambda_{JT})$ or epikernel $E(G, \Lambda_{JT})$ subgroups of the HS parent group G . Kernels contain the symmetry operations of G that leave the Λ_{JT} representation invariant. The symmetry operations of epikernels leave invariant only some components of the degenerate Λ_{JT} representation.

The epikernel principle was originally formulated for the systems in degenerate electron states only [5,6], but it has been successfully extended (except Eq. (6)) to pseudodegenerate electron states as well [7]. Its drawback is in the restriction to JT active coordinates that have been derived within perturbation theory for the linear Taylor expansion of the perturbation only. This method might offer incomplete results in some cases (e.g., in systems with C_5 rotations) [7].

The method of step-by-step symmetry descent [8,9] is based on consecutive splitting of a degenerate electron state within a JT symmetry descent. The corresponding multidimensional representation can be split within symmetry descent to an immediate subgroup of the parent HS group G . If the structure corresponding to this subgroup is in a nondegenerate electron state, it is JT stable and the symmetry descent stops. If the structure corresponding to an immediate subgroup of G is in a degenerate electron state described by a multidimensional representation (a JT unstable structure), the symmetry descent continues, and the whole procedure is repeated. As every group can have several immediate subgroups, various symmetry descent paths are possible and the JT stable structures can correspond to various LS symmetry groups. The only condition is its nondegenerate electron state (i.e. one-dimensional representation) obtained by splitting the degenerate electron state (i.e., multidimensional representation) of the HS structure of the parent group G .

3. Results

The highest possible structures of $[dmaphPcAg]^q$ complexes are of the D_{4h} symmetry group with side phenyl groups perpendicular to the central phtalocyanine plane (Figure 2). Because of the great number of possible mutual orientations of dimethyl amino phenyl groups in less symmetric structures, we restricted our study to the stable structures of maximal symmetry group only. Another restriction is implied by the inability of standard DFT methods to optimize the atomic configurations in degenerate electron states [10]. The results of the geometry optimizations of the $^m[dmaphPcAg]^q$ complexes with total charges $q = +1 \rightarrow -2$ in the two lowest spin states m are presented in Table 1. It is interesting that the $[dmaphPcAg]^q$ complexes in the triplet spin state are more stable than these ones with the same charge in the singlet spin state. $^3[dmaphPcAg]$ of D_2 symmetry is even the most stable complex under study. It must be mentioned that the use of an unrestricted 'broken symmetry' treatment [11] results in zero spin populations and does not reduce the energy of the systems studied. Therefore, only the restricted Kohn-Sham formalism has been used in subsequent TD-DFT calculations of our complexes in singlet ground states.

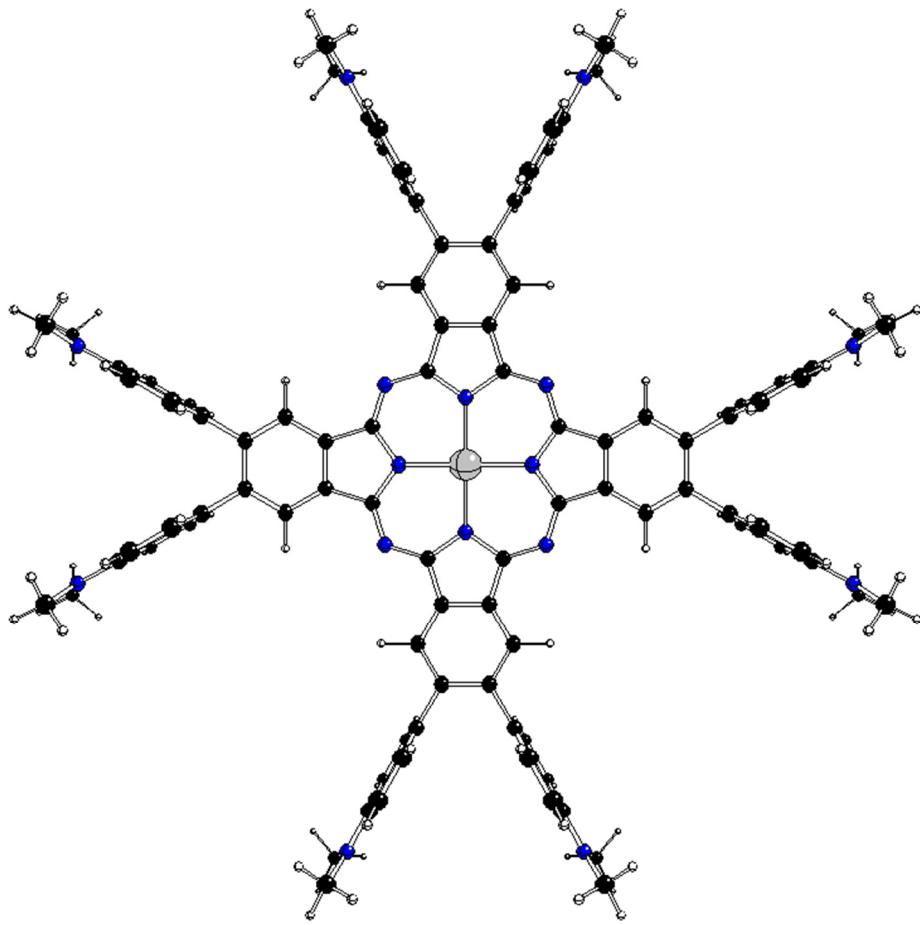


Figure 2. Optimized D_{4h} structure of ${}^0[dmaphPcAg]$ (C – black, N – blue, H – white, Ag – grey).

Table 1. Charge q , spin multiplicity m , symmetry group G , representation of the ground electron state Γ_0 , DFT energy E_{DFT} , JT stabilization energy E_{JT} , representations Λ_{im} and wavenumbers ν_{im} of imaginary vibrations, kernel $K(D_{4h}, \Lambda_{im})$ and epikernel $K(D_{4h}, \Lambda_{im})$ subgroups of D_{4h} , and representations of relevant PJT excited states Γ_{exc} of ${}^m[dmaphPc]^q$ complexes under study (the preserved symmetry elements in the kernel and epikernel subgroups are in parentheses). The most stable structure is shown in bold.

q	m	G	Γ_0	E_{DFT} [Hartree]	E_{JT} [eV]	Λ_{im}	ν_{im} [cm ⁻¹]	K(D_{4h}, Λ_{im})	E(D_{4h}, Λ_{im})	Γ_{exc}
+1	1	D_{4h}	${}^1A_{1g}$	-4734.55067	-	b _{1u}	-48	$D_{2d}(C_2')$		B _{1u}
						2e _g	-47, -31	C ₁	$C_{2h}(C_2')$, $C_{2h}(C_2'')$	E _g
						a _{1u}	-46	D ₄		A _{1u}
						a _{2u}	-31	C _{4v}		A _{2u}
						b _{2u}	-31	$D_{2d}(C_2'')$		B _{2u}
+1	1	D_4	1A_1	-4734.58352	0.894	-	-			
+1	3	D_{4h}	${}^3B_{1u}$	-4734.54698	-	b _{1u}	-18	$D_{2d}(C_2')$		A _{1g}
						e _g	-18	C ₁	$C_{2h}(C_2')$, $C_{2h}(C_2'')$	E _u
						a _{1u}	-18	D ₄		B _{1g}
+1	3	D_4	3B_1	-4734.58550	1.048	-	-			
0	2	D_{4h}	${}^2B_{1g}$	-4734.74708	-	b _{1u}	-42	$D_{2d}(C_2')$		A _{1u}
						e _g	-42	C ₁	$C_{2h}(C_2')$, $C_{2h}(C_2'')$	E _g
						a _{1u}	-41	D ₄		B _{1u}

						a _{2u}	-23	C _{4v}	B _{2u}
0	2	D ₄	² B ₁	-4734.77283	0.701	3b _{2u}	-23(3x)	D _{2d} (C _{2''})	A _{2u}
0	4	D ₂	⁴ B ₂	-4734.73113	?	-	-		
-1	1	D ₂	¹ A	-4734.79846	?	-	-		
-1	3	D ₂	³ B ₂	-4734.83355	?	-	-		
-2	2	D ₂	² B ₁	-4734.80520	?	-	-		
-2	4	D _{4h}	⁴ B _{1u}	-4734.77355	-	b _{1u}	-47	D _{2d} (C _{2'})	A _{1g}
						2e _g	-46,-27	C ₁	C _{2h} (C _{2'}), C _{2h} (C _{2''})
						a _{1u}	-45	D ₄	B _{1g}
						a _{2u}	-27	C _{4v}	B _{2g}
						b _{2u}	-27	D _{2d} (C _{2''})	A _{2g}
-2	4	D ₄	⁴ B ₁	-4734.80581	0.878	-	-		

Further inspection of Table 1 shows that the studied complexes can be divided into two categories:

- i) Category I contains complexes ¹[dmaphPcAg]⁺, ³[dmaphPcAg]⁺, ²[dmaphPcAg]⁰ and ⁴[dmaphPcAg]²⁻ with optimized structures of D_{4h} (unstable) and D₄ (stable) symmetry groups.
- ii) Category II contains complexes ⁴[dmaphPcAg]⁰, ¹[dmaphPcAg]⁺, ³[dmaphPcAg]⁻ and ²[dmaphPcAg]²⁻ where only their stable optimized structures of the D₂ symmetry group were found, while the D_{4h} optimized structures were absent. This can be explained by the electron configurations of the D_{4h} complexes in Table 2. We may conclude that the category II complexes should contain partially occupied e_g molecular orbitals, which implies E_g or E_u ground electron states. Hence, they are not accessible by standard DFT methods.

Table 2. Charge q, spin multiplicity m, electron configuration, and ground electron state representation Γ_0 of studied ^m[dmaphPc]^q complexes of D_{4h} symmetry group.

q	m	Electron configuration	Γ_0
+1	1	...(b _{2g}) ² (e _u) ⁴ (a _{2g}) ² (b _{1g}) ⁰ (e _g) ⁰ (b _{1u}) ⁰ ...	¹ A _{1g}
+1	3	α : ... (b _{1g}) ¹ (a _{2g}) ¹ (e _u) ² (b _{2g}) ¹ (e _g) ⁰ (b _{1u}) ⁰ ... β : ... (e _u) ² (b _{2g}) ¹ (a _{1u}) ⁰ (e _g) ⁰ (b _{1g}) ⁰ (b _{1u}) ⁰ ...	³ B _{1u}
0	2	α : ... (e _u) ² (b _{2g}) ¹ (b _{1g}) ¹ (a _{1u}) ¹ (e _g) ⁰ (b _{1u}) ⁰ ... β : ... (e _u) ² (b _{2g}) ¹ (a _{1u}) ¹ (e _g) ⁰ (b _{1g}) ⁰ (b _{1u}) ⁰ ...	² B _{1g}
0	4	?	⁴ E _g or ⁴ E _u
-1	1	?	¹ E _g or ¹ E _u
-1	3	?	³ E _g or ³ E _u
-2	2	?	² E _g or ² E _u
-2	4	α : ... (e _g) ² (b _{2g}) ¹ (a _{1u}) ¹ (b _{1g}) ¹ (e _g) ² (b _{2u}) ⁰ ... β : ... (e _g) ² (a _{2u}) ¹ (a _{1u}) ¹ (e _g) ⁰ (a _{2u}) ⁰ (b _{2u}) ⁰ ...	⁴ B _{1u}

3.1. Category I complexes

The optimized D_{4h} structures of these complexes are unstable due to several imaginary vibrations of Λ_{im} representations (Table 1) that coincide with the JT active coordinates. The JT stabilization energies E_{JT} correspond to D_{4h} \rightarrow D₄ symmetry decrease. Stable D₄ structures with equally rotated phenyl rings (Figure 3) and without any imaginary vibration correspond to the K(D_{4h}, Λ_{im}) kernel subgroups for the coordinate of the a_{1u} representation. As indicated by its wavenumber ν_{im} , the energies of the corresponding vibrations are comparable with the highest energy ones in all category I complexes. The optimized structures of D_{2d} and C_{4v} symmetries are not stable (not presented), and hence only the D₄ ones fulfill the condition of the stable structure of the highest symmetry group.

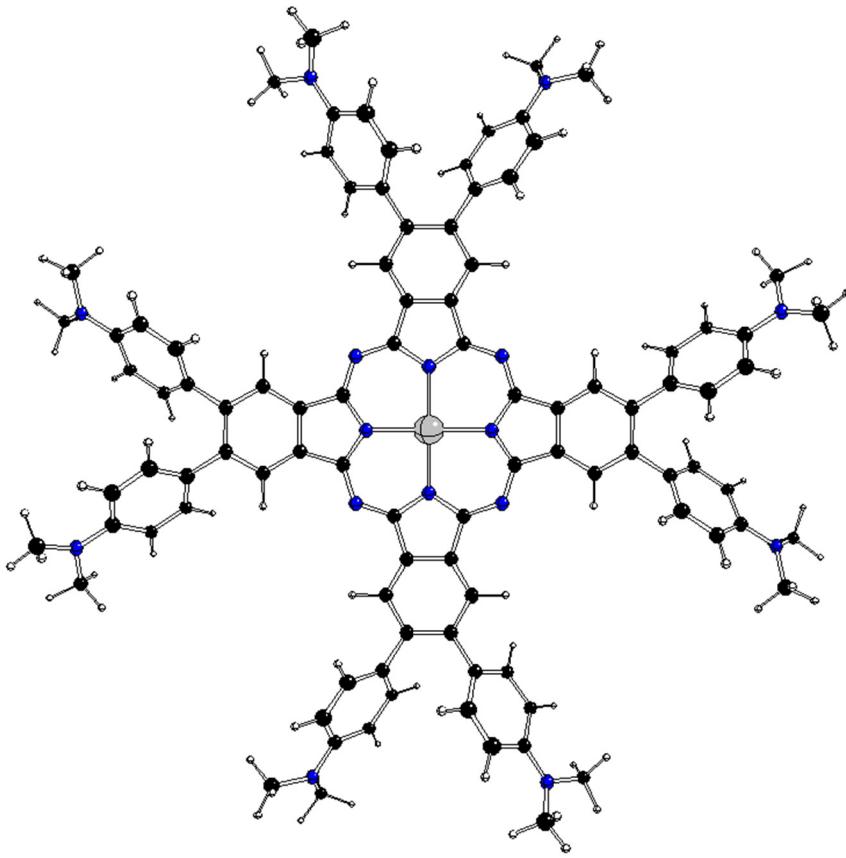


Figure 3. Optimized D₄ structure of ²[dmaphPcAg]⁰ (see Fig. 2 for atom notation).

For known ground state Γ_0 and JT coordinate Λ_{im} representations the Eqs. (4) and (5) enable to determine the excited state representations Γ_{exc} (see Table 1) interacting with the ground electron state in D_{4h} structures of our complexes. The comparison of the TD-DFT calculated electron states in the corresponding D_{4h} and D₄ structures (Table 3) shows that the energy difference E_{exc} between the PJT interacting states increases after symmetry descent as a consequence of their vibronic interaction. This confirms the correct assignment of the corresponding states in both groups because the standard treatment based on similarity of their oscillator strengths f is hardly usable in our cases. The ground states in the D_{4h} structures also correspond to those in their D₄ subgroups.

We can see (Table 3) that the PJT active excited states in the D_{4h} structures are relatively high. This indicates that their excitation energies are less important for possible vibronic interactions than the energies of JT active coordinates.

Table 3. Charge q , spin multiplicity m , symmetry group G , ground electron state representation Γ_0 , representations Γ_{exc} , excitation energies E_{exc} and oscillator strengths f of the low excited electron states of the studied ${}^m[\text{dmaphPc}]^q$ complexes in D_{4h} and D₄ symmetry groups. The excited states that interact with the ground states are in bold.

q	m	G	Γ_0	Γ_{exc}	$E_{\text{exc}} [\text{eV}]$	f	G	Γ_0	Γ_{exc}	$E_{\text{exc}} [\text{eV}]$	f
+1	1	D _{4h}	¹ A _{1g}	¹ A _{2g}	0.156	0.000	D ₄	¹ A ₁	¹ B ₁	0.167	0.000
				¹ E _u	0.158	0.002			¹ B ₂	0.255	0.000
				¹ B _{2g}	0.159	0.000			¹ E	0.259	0.000
				¹ B _{1g}	0.349	0.000			¹ A ₂	0.267	0.000
				² E _u	0.353	0.081			² E	0.631	0.014
				¹ B _{1u}	0.377	0.000			¹ A ₁	0.642	0.000
				¹ A _{1g}	0.487	0.000			² B ₁	0.858	0.000

+1	3	D_{4h}	${}^3B_{1u}$	1E_g	1.010	0.000		3E	1.187	0.050	
				${}^1A_{1u}$	1.010	0.000		2A_1	1.192	0.001	
				${}^1B_{1u}$	1.010	0.000		2A_2	1.200	0.000	
				${}^1B_{2g}$	0.011	0.000	D_4	3B_1	3E	0.188	0.007
				${}^1A_{2g}$	0.015	0.001			3B_2	0.190	0.000
				1E_u	0.016	0.001			3A_2	0.195	0.000
				${}^1A_{1g}$	0.235	0.000			1A_1	0.600	0.000
				2E_u	0.235	0.014			2E	0.617	0.298
				${}^1B_{2u}$	0.239	0.000			1B_1	0.779	0.000
				2E_u	1.255	0.000			3E	1.244	0.001
0	2	D_{4h}	${}^2B_{1g}$	3E_u	1.327	0.003			4E	1.391	0.033
				1E_g	1.493	0.008			2B_1	1.400	0.000
				2E_u	1.195	0.000	D_4	2B_1	1E	1.157	0.000
				2E_g	1.306	0.000			2E	1.305	0.000
				${}^2B_{1u}$	2.014	0.000			3E	1.901	0.624
				2E_u	2.050	0.710			1B_2	1.942	0.000
				2E_g	2.140	0.000			2A_2	1.944	0.000
				${}^2B_{2u}$	2.140	0.000			4E	1.956	0.004
				${}^2A_{2u}$	2.140	0.000			2A_2	1.969	0.000
				3E_g	2.163	0.000			1A_1	2.055	0.000
-2	4	D_{4h}	${}^4B_{1u}$	${}^2B_{2u}$	2.164	0.000			3A_2	2.056	0.000
				${}^2A_{2u}$	2.164	0.000			1B_1	2.059	0.001
				4E_g	0.957	0.000	D_4	4B_1	4E	0.888	0.191
				${}^4A_{2u}$	0.976	0.000			4B_1	1.356	0.000
				${}^4B_{2u}$	0.978	0.000			2E	1.360	0.010
				2E_g	1.025	0.000			4A_1	1.360	0.000
				${}^4A_{1u}$	1.042	0.000			3E	1.396	0.010
				${}^4B_{1u}$	1.048	0.000			4A_2	1.415	0.000
				3E_g	1.118	0.110			4B_2	1.417	0.000
				${}^4A_{1g}$	1.495	0.000			4E	1.436	0.012
				${}^4B_{1g}$	1.495	0.000			2B_2	1.472	0.001
				4E_u	1.496	0.000			4A_2	1.481	0.000
				${}^2A_{1u}$	1.501	0.000			3B_1	1.523	0.000

3.2. Category II complexes

As mentioned above, the ground state of the D_{4h} structures of these complexes is double degenerate (E_g or E_u representations) and only the stable D_2 structures (Figure 4) were obtained by geometry optimizations. Possible representations of the corresponding JT active coordinates can be obtained by the symmetric direct products for the HS group

$$[E_g \otimes E_g]^+ = [E_u \otimes E_u]^+ = A_{1g} \oplus B_{1g} \oplus B_{2g} \quad (6)$$

The full-symmetric A_{1g} coordinate does not change the symmetry of the structure (i.e. cannot be JT active) and the kernels

$$K(D_{4h}, b_{1g}) = D_{2h}(C_2') \quad (7)$$

$$K(D_{4h}, b_{2g}) = D_{2h}(C_2'') \quad (8)$$

do not explain the existence of the optimized D_2 structure. Therefore, the method of the epikernel principle [5,6] cannot explain the $D_{4h} \rightarrow D_2$ symmetry descent.

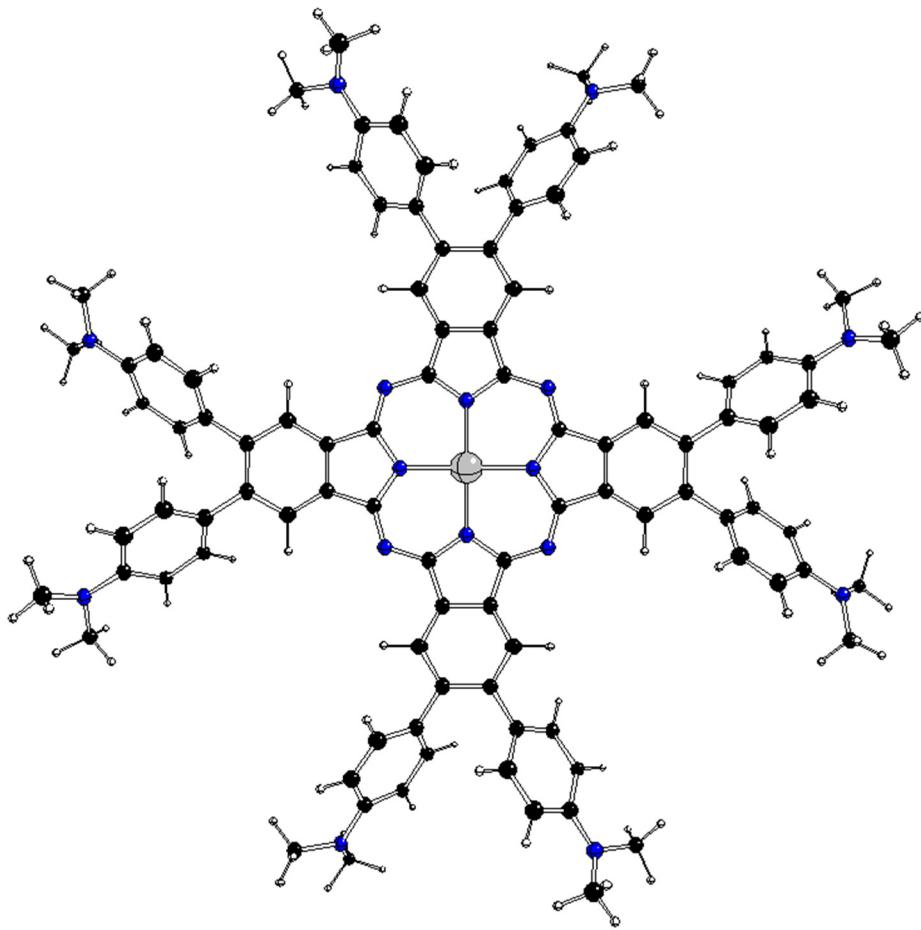


Figure 4. Optimized D_2 structure of ${}^1[\text{dmaphPcAg}]^-$ (see Figure 2 for atom notation).

The method of step-by-step symmetry descent [8,9] for the structures of the D_{4h} symmetry group in double degenerate electron states is based on the scheme in Figure 5. Except D_{2h} , all immediate subgroups of the D_{4h} group (i. e. D_4 , D_{2d} , C_{4v} and C_{4h}) are JT unstable because of preserved electron degeneracy. After the removal of the C_4 axis from the D_4 group we obtain its immediate subgroup D_2 , which is JT stable because the degeneracy is removed here. Alternatively, the D_2 group can be obtained by symmetry descent through JT unstable D_{2d} group with preserved electron degeneracy. The structures of the C_4 and S_4 symmetry groups preserve electron degeneracy and therefore cannot be stable. We have not found any stable structure of D_{2h} , C_{2v} , or C_{2h} symmetry groups by geometry optimization. Therefore, the stable D_2 structures meet the condition of maximal groups for category II complexes.

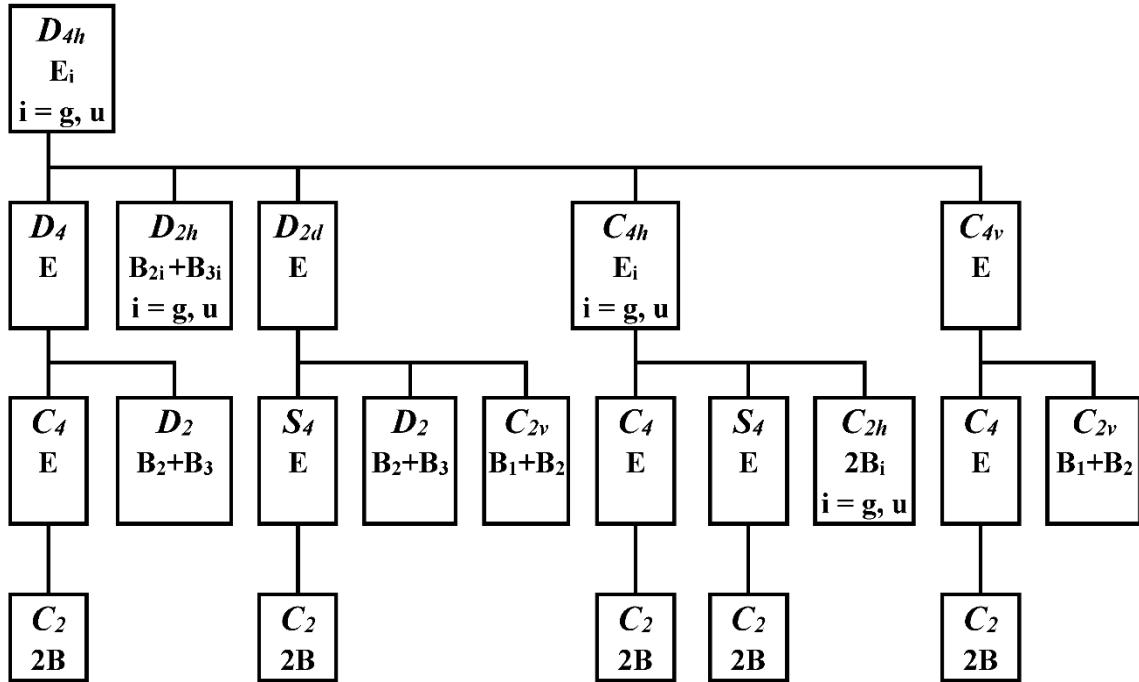


Figure 5. Possible symmetry descent paths of D_{4h} structures in double degenerate electron states [9]. The top and bottom lines of individual rectangles denote symmetry groups and the corresponding irreducible representations, respectively.

During the symmetry descent from D_{4h} to D_2 group the double degenerate representation is split into the nondegenerate B_2 and B_3 ones

$$E_g \text{ or } E_u (D_{4h}) \rightarrow E (D_4 \text{ or } D_{2d}) \rightarrow B_2 \oplus B_3 (D_2) \quad (9)$$

None of these representations corresponds to the calculated ground electron state of the stable D_2 structures. (Table 4). This discrepancy can be explained by the above-mentioned HPJT effect and the ground state of the D_2 structure corresponds to the lower PJT interacting excited state in its supergroup. In our case, the situation is complicated by the fact that D_2 is not an immediate subgroup of the D_{4h} group. Therefore, three possible two-step symmetry descent paths are possible:

$$\text{i) } D_{4h} \xrightarrow{a_{1u}} D_4 \xrightarrow{b_1 \text{ or } b_2} D_2 \quad (10)$$

$$\text{ii) } D_{4h} \xrightarrow{b_{1g} \text{ or } b_{2g}} D_{2h} \xrightarrow{a_u} D_2 \quad (11)$$

$$\text{iii) } D_{4h} \xrightarrow{b_{1u} \text{ or } b_{2u}} D_{2d} \xrightarrow{b_1} D_2 \quad (12)$$

Based on group-subgroup relations we can assign the electron state representations of the D_2 symmetry group to the corresponding D_4 , D_{2h} or D_{2d} ones despite there can be several alternatives. The same holds for the D_{4h} to D_4 , D_{2h} or D_{2d} symmetry descent. For known representations of ground states and JT active coordinates, it might be possible to determine the HPJT excited state representations according to Eq. (4). For the two-step symmetry descent there are too many possibilities where almost all excited-state representations (except two-dimensional) might be involved. Therefore, we shall not deal with this problem.

Table 4. Charge q , spin multiplicity m , representations of the ground electron state Γ_0 and of the excited states Γ_{exc} , excitation energies E_{exc} and oscillator strengths f of low excited electron states of stable ${}^m[\text{dmaphPc}]^q$ complexes under study in the D_2 symmetry group. The irreducible representations obtained by splitting the two-dimensional representations of the degenerate ground state in D_{4h} structures are in bold.

q	m	Γ_0	Γ_{exc}	E_{exc} [eV]	f	q	m	Γ_0	Γ_{exc}	E_{exc} [eV]	f
0	4	${}^4\text{B}_2$	${}^1\text{B}_1$	0.349	0.000	-1	1	${}^1\text{A}$	${}^1\text{B}_2$	0.523	0.000
			${}^1\text{B}_3$	0.814	0.012				${}^1\text{B}_1$	0.539	0.000
			${}^2\text{B}_1$	0.829	0.000				${}^1\text{B}_3$	0.815	0.000
			${}^1\text{B}_2$	0.927	0.006				${}^2\text{B}_2$	1.337	0.023
			${}^3\text{B}_1$	0.948	0.000				${}^2\text{B}_3$	1.478	0.028
			${}^2\text{B}_3$	1.253	0.000				${}^3\text{B}_2$	1.551	0.005
			${}^2\text{B}_2$	1.254	0.213				${}^4\text{B}_2$	1.793	0.809
			${}^1\text{A}$	1.291	0.000				${}^3\text{B}_3$	1.965	0.018
			${}^3\text{B}_3$	1.356	0.164				${}^1\text{A}$	2.056	0.000
			${}^2\text{A}$	1.423	0.000				${}^4\text{B}_3$	2.097	0.011
-1	3	${}^3\text{B}_2$	${}^1\text{B}_1$	0.272	0.000	-2	2	${}^2\text{B}_1$	${}^1\text{B}_1$	0.048	0.000
			${}^1\text{B}_3$	1.256	0.000				${}^2\text{B}_1$	0.377	0.000
			${}^1\text{B}_2$	1.350	0.021				${}^1\text{B}_2$	0.900	0.007
			${}^2\text{B}_3$	1.356	0.014				${}^2\text{B}_2$	1.095	0.283
			${}^2\text{B}_2$	1.796	0.792				${}^1\text{B}_3$	1.112	0.306
			${}^3\text{B}_3$	1.835	0.007				${}^3\text{B}_2$	1.168	0.000
			${}^4\text{B}_3$	1.987	0.012				${}^1\text{A}$	1.343	0.000
			${}^1\text{A}$	1.993	0.000				${}^4\text{B}_2$	1.348	0.002
			${}^2\text{B}_1$	2.000	0.000				${}^2\text{A}$	1.362	0.000
			${}^2\text{A}$	2.092	0.000				${}^2\text{B}_3$	1.367	0.002

4. Methods

We have performed geometry optimization of the complexes ${}^m[\text{dmaphPcAg}]^q$ with charges $q = +1 \rightarrow -2$ in the two lowest spin states (singlet to quartet) with spin multiplicities m within the D_{4h} symmetry and its subgroups. In agreement with our previous study [1], B3LYP hybrid functional [12], GD3 dispersion correction [13], cc-pVDZ-PP pseudopotential and basis set for Ag [14] and cc-pVDZ basis sets for remaining atoms [15] were used. The optimized structures were tested on the number of imaginary vibrations. Excited states (up to 50) were calculated for every optimized structure using time-dependent DFT (TD-DFT) treatment [16,17] analogously to our previous studies [1,18,19]. All calculations were performed with Gaussian16 (Revision B.01) software [20]. MOLDRAW (<https://www.moldraw.software.informer.com>, accessed on 9 September 2019) software [21] was used for visualization and geometry modification purposes. Finally, a group-theoretical analysis of the obtained results was carried out using the methods of the epikernel principle [5–7] and of step-by-step symmetry descent [8,9].

5. Conclusions

To shed more light on the photopolymerization action of the Ag(II) complex with dimethylamino phenyl-substituted phtalocyanine ${}^2[\text{dmaphPcAg}]^0$, we have performed a quantum-chemical model study of possible reaction intermediates $[\text{dmaphPcAg}]^q$ with charges $q = +1 \rightarrow -2$ with the aim to explain the possible role of the JT effect. Group-theoretical analysis of the obtained results shows that the complexes under study are of two categories.

Stable structures of maximal symmetry of ${}^1[\text{dmaphPcAg}]^+$, ${}^3[\text{dmaphPcAg}]^+$, ${}^2[\text{dmaphPcAg}]^0$ and ${}^4[\text{dmaphPcAg}]^{2-}$ complexes (category I) correspond to the D_4 group as a consequence of the PJT effect within the unstable D_{4h} structure. On the other hand, complexes ${}^4[\text{dmaphPcAg}]^0$, ${}^1[\text{dmaphPcAg}]^-$, ${}^3[\text{dmaphPcAg}]^-$ and ${}^2[\text{dmaphPcAg}]^{2-}$ (category II) with double degenerate electron ground states in

(JT unstable) D_{4h} symmetry structures undergo a symmetry descent to stable structures corresponding to maximal D_2 symmetry not because of a simple JT effect, but due to HPJT effect. The most stable reaction intermediate in the supposed photoinitiation reaction [1] is surprisingly $^3[\text{dmaphPcAg}]$ (a singlet electron state was expected). Therefore, the reduction of $^2[\text{dmaphPcAg}]^0$ photoinitiator (D_4 symmetry) to $^3[\text{dmaphPcAg}]$ intermediate (D_2 symmetry) must be significantly affected by vibronic interactions (PJT and HPJT effects). Their influence on reaction rates and thermodynamics must be investigated in solutions.

The presented study shows how group-theoretical treatment can be profitable by solving chemical problems for large molecules. The method of epikernel principle [5–7] is restricted to JT active coordinates based on perturbation theory and thus grants incomplete results but can also be used for the PJT effect. The method of step-by-step symmetry descent [8,9] based on splitting degenerate electron states during symmetry descent is more universal but not suitable for the PJT effect. We have shown the usefulness of the combination of both methods. Further theoretical studies in this field are welcome.

Author Contributions: Investigation, writing—original draft preparation, writing—review and editing, M.B. All authors have read and agreed to the published version of the manuscript.

Funding: The work has been supported by the Slovak Research and Development Agency (no. APVV-19-0087), by the Slovak Scientific Grant Agency VEGA (no. 1/0139/20), and by Ministry of Education, Science, Research and Sport of the Slovak Republic within the scheme “Excellent research teams”.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Acknowledgments: The authors thank the HPC center at the Slovak University of Technology in Bratislava, which is a part of the Slovak Infrastructure of High Performance Computing (SIVVP project ITMS 26230120002 funded by the European Region Development Funds) for the computational time and resources made available.

Conflicts of Interest: The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Sample Availability: Not applicable.

References

1. Breloy, L.; Alcay, Y.; Yilmaz, I.; Breza, M.; Bourgon, J.; Brezová, V.; Yagci, Y.; Versace, D.-L. Dimethyl amino phenyl substituted silver phthalocyanine as a UV- and visible-light absorbing photoinitiator: in situ preparation of silver/polymer nanocomposites. *Polym. Chem.* **2021**, *12*, 1273–1285.
2. Jahn, H. A.; Teller, E. Stability of polyatomic molecules in degenerate electronic states. I. Orbital degeneracy. *Proc. R. Soc. London A* **1937**, *161*, 220–235.
3. Bersuker, I. B. Pseudo-Jahn–Teller Effect—A Two-State Paradigm in Formation, Deformation, and Transformation of Molecular Systems and Solids. *Chem. Rev.* **2013**, *113*, 1351–1390.
4. Bersuker I.B. Recent Developments in the Jahn–Teller Effect Theory. In *The Jahn–Teller Effect. Fundamentals and Implications for Physics and Chemistry*; Köppel, H., Yarkony, D.R., Barentzen, H., Eds.; Springer, 2009; pp. 3–24. ISBN 978-3642034312.
5. Ceulemans, A.; Beyens, D.; Vanquickenborne, L. G. Symmetry aspects of Jahn–Teller activity: structure and reactivity. *J. Am. Chem. Soc.* **1984**, *106*, 5824–5837.
6. Ceulemans, A.; Vanquickenborne, L. G. The Epikernel Principle. *Struct. Bonding* **1989**, *71*, 125–159.
7. Breza, M. Group-Theoretical Treatment of Pseudo-Jahn–Teller Systems. In *Vibronic Interactions and the Jahn–Teller Effect: Theory and Application*. (Prog. Theor. Chem. Phys. B 23); Atanasov, M., Daul, C., Tregenna-Piggott, P.L.W., Eds.; Springer: Dordrecht, The Netherlands; Berlin/Heidelberg, Germany; London, UK; New York, NY, USA, 2012; pp. 59–82. ISBN 1567-7354.
8. Pelikán, P.; Breza, M. Classification of the possible symmetries of the Jahn–Teller systems. *Chem. Papers* **1984**, *39*, 255–270.
9. Breza, M. Group-Theoretical Analysis of Jahn–Teller Systems. In *The Jahn–Teller Effect. Fundamentals and Implications for Physics and Chemistry*; Köppel, H., Yarkony, D.R., Barentzen, H., Eds.; Springer, 2009; pp. 51–76. ISBN 978-3642034312.

10. Kaplan, I. G. Problems in DFT with the total spin and degenerate states. *Int. J. Quantum Chem.* **2007**, *107*, 2595–2603.
11. Schurkus, H.F.; Chan, G. K.-L.; Chen, G.-T.; Cheng, H.-P.; Stanton, J.F. Theoretical prediction of magnetic exchange coupling constants from broken-symmetry coupled cluster calculations *J. Chem. Phys.* **2020**, *152*, 234115.
12. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.*, **1993**, *98*, 5648–5652.
13. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parameterization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.*, **2010**, *132*, 154104.
14. Pritchard, B.P.; Altarawy, D.; Didier, B.; Gibson, T.D.; Windus, T.L. New Basis Set Exchange: An Open, Up-to-Date Resource for the Molecular Sciences Community. *J. Chem. Inf. Model.* **2019**, *59*, 4814–4820.
15. Dunning Jr., T.H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.*, **1989**, *90*, 1007–1023.
16. Bauernschmitt, R.; Ahlrichs, R. Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory. *Chem. Phys. Lett.* **1996**, *256*, 454–464.
17. Scalmani, G.; Frisch, M. J.; Mennucci, B.; Tomasi, J.; Cammi, R.; Barone, V. Geometries and properties of excited states in the gas phase and in solution: theory and application of a time-dependent density functional theory polarizable continuum model. *J. Chem. Phys.* **2006**, *124*, 94107.
18. Štellerová, D.; Lukeš, V.; Breza, M. How does pseudo-Jahn-Teller effect induce the photoprotective potential of curcumin? *Molecules* **2023**, *28*, 2946.
19. Štellerová, D.; Lukeš, V.; Breza, M. On the Potential Role of (Pseudo-) Jahn-Teller effect in Membrane Transport Processes: Enniatin B and Beauvericin. *Molecules* **2023**, *28*, 6264.
20. Frisch, G.W.M.J.; Schlegel, B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; Li, X.; et al. *Gaussian 16, Revision B.01*; Gaussian, Inc.: Wallingford, CT, USA, 2016.
21. Ugliengo, P. MOLDRAW: A Program to Display and Manipulate Molecular and Crystal Structures, University Torino, Torino. 2012. Available online: <https://www.moldraw.software.informer.com> (accessed on 9 September 2019).

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.