Pseudo-Jahn-Teller Effect in Deprotonated Dimethyl Amino Phenyl Substituted Phthalocyanine

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INTRODUCTION

Phtalocyanines (PcH_2) are used as photosensitizers, dyes, pigments, fluorescent and electroactive molecules for biomedical and industrial applications.

Breloy *et al*. [1] synthesized a novel dimethyl amino phenyl substituted phthalocyanine ($dmaphPcH_2$) and its Ag(II) complex ($[dmaphPcAg]^0$, see Fig. 1) used as a visible light-absorbing photoinitiator for free-radical and cationic polymerizations.

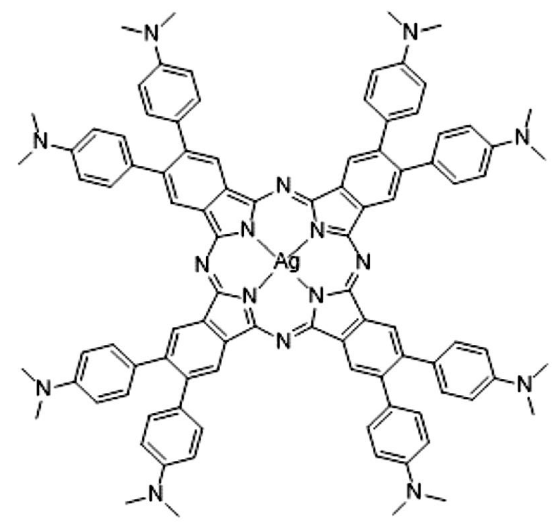

Figure 1. Structure of $[dmaphPcAg]^0$ [1]

Irradiation of the $[dmaphPcAg]^0$ solution led to the reduction of Ag(II) to Ag(I) and simultaneously generated the nitrogen-centered radical. In the next step, Ag nanoparticles and aromatic carbon-centered radicals were formed. The proposed photoinitiation mechanisms under light irradiation suppose the existence of $[dmaphPc]^0$, Ag^0 and $[dmaphPcAg]^q$ entities, q = -1, 0 or +1. DFT calculations indicate a $D_4 \rightarrow D_2$ symmetry descent due to the Jahn-Teller effect in Ag complexes.

The intermediate deprotonated $[dmaphPc]^q$ species, q = -2 → 0, are formed during the above redox processes. Our study deals with their DFT study and group-theoretical analysis from the point of view of the Pseudo-Jahn-Teller (PJT) effect in terms of the epikernel principle method [2, 3] with the aim to shed more light on the processes in the above systems. Our study is restricted to the symmetry descent from the highest possible D_{4h} structures to the stable structures of its maximal symmetry subgroup due to a great number of possible conformations of dimethyl amino phenyl groups.

METHOD

Standard B3LYP [4] geometry optimization with Grimme's GD3 dispersion correction [5] of $[dmaphPc]^q$, q = -2 to 0, in (singlet or doublet) ground spin states using the cc-pVDZ basis sets [6] was performed within D_{4h} and lower symmetry groups. The optimized structures were checked on imaginary vibrations by vibrational analysis. The excited-state energies with the corresponding electron transitions were evaluated using the time-dependent DFT method [7]. All calculations were performed using the Gaussian16 [8] program package.

THEORETICAL BACKGROUND

The epikernel-principle method for pseudodegenerate states [2, 3] is based on the Jahn-Teller active distortion coordinate Q of Λ representation for pseudodegenerate electron states Ψ_1 and Ψ_2 of Γ_1 and Γ_2 representations, respectively, within the parent symmetry group G. Λ is the non-totally symmetric part of the symmetrized direct product $[\Gamma \otimes \Gamma]$ which corresponds to a non-vanishing value of $< \Psi_1 \left| \frac{\partial \hat{H}}{\partial Q} \right| \Psi_2 >$ integrals where $\hat{H}$ denotes Hamiltonian. According to the epikernel principle, the extrema of a JT energy surface correspond to the kernel K(G, Λ) or epikernel E(G, Λ) subgroups of the parent group G. Kernels contain symmetry operations that leave the Λ representation invariant, whereas epikernels leave invariant only some components of the degenerate Λ representation. The energy difference between the high-symmetry unstable and low-symmetry (stable) structures of the same compound is denoted as the Jahn-Teller stabilization energy E_{JT}.

ACKNOWLEDGEMENT

Science and Technology Assistance Agency of Slovak Republic (contract No. APVV-19-0087) and Slovak Grant Agency VEGA (contract No. 1/0139/20) are acknowledged for financial support.

RESULTS

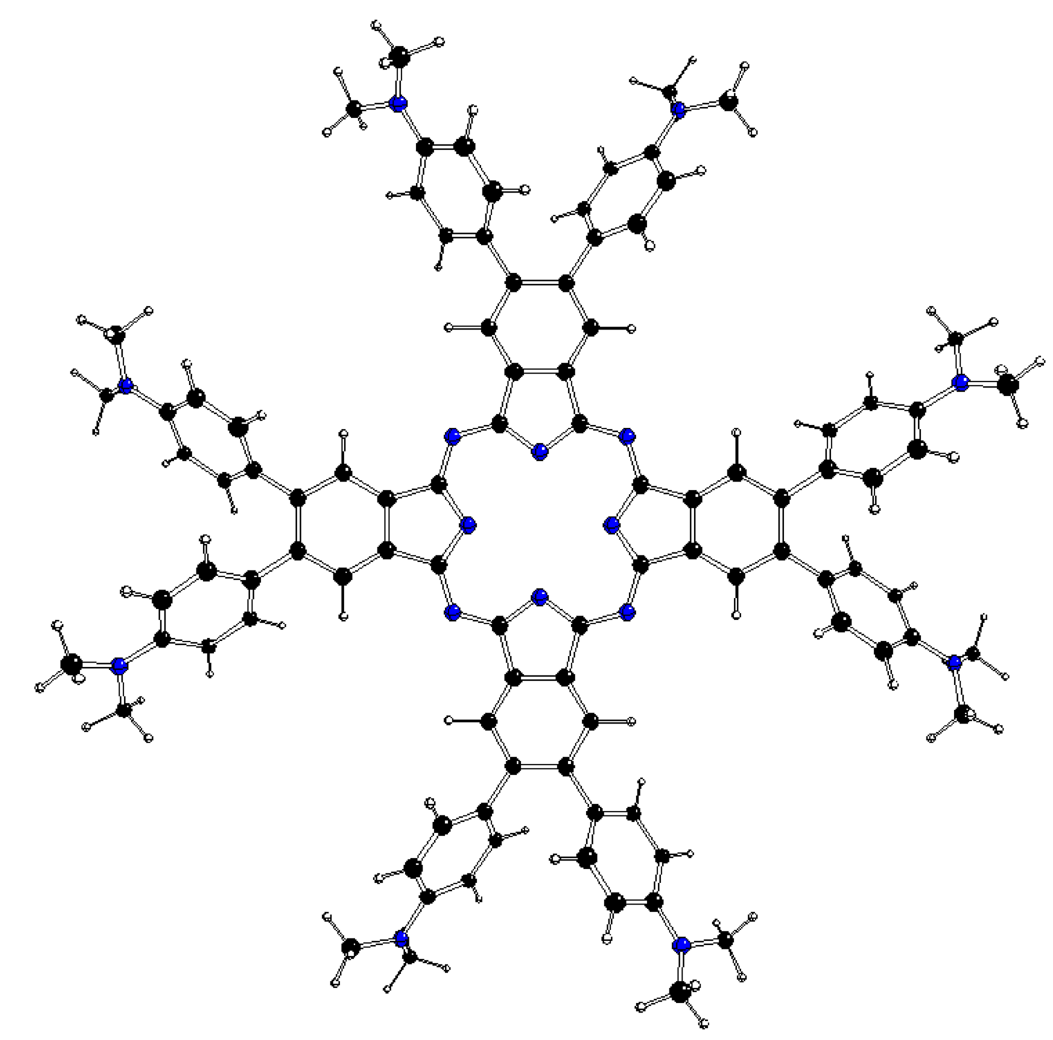

Figure 2. Optimized stable structure of $[dmaphPc]^{2-}$ of D_4 symmetry.

Table 1. Ground state Γ_1, DFT energy E_{DFT}, representations Λ_{im}, corresponding wavenumbers ν_{im}, kernels and epikernels of imaginary vibrations in optimized $[dmaphPc]^q$ geometries of various groups G.

$^1[dmaphPc]^{2-}$

G	Γ_0	E_{DFT} [Hartree]	E_{JT} [eV]	Λ_{im}	ν_{im} [cm^{-1}]	K(G, Λ_{im})	E(G, Λ_{im})
D_{4h}	$^1A_{1g}$	-4587.70938	0.000	b_{1u}	-44	$D_{2d}(C_2')$	
				e_g	-43	C_1	$C_{2h}(C_2')$, $C_{2h}(C_2'')$
				a_{1u}	-42	D_4	
				a_{2u}	-25	C_{4v}	
				b_{2u}	-24 (3×)	$D_{2d}(C_2'')$	
D_4	$^1A_1$	-4587.73758	0.767	-		-	

$^2[dmaphPc]^{-}$

G	Γ_0	E_{DFT} [Hartree]	E_{JT} [eV]	Λ_{im}	ν_{im} [cm^{-1}]	K(G, Λ_{im})	E(G, Λ_{im})
D_{4h}	$^2A_{1u}$	-4587.70651	0.000	b_{1u}	-42	$D_{2d}(C_2')$	
				e_g	-41	C_i	$C_{2h}(C_2')$, $C_{2h}(C_2'')$
				a_{1u}	-40	D_4	
				b_{2u}	-22(4×), -4	$D_{2d}(C_2'')$	
D_4	$^2A_1$	-4587.73130	0.025	b_2	-4	$D_2(C_2'')$	
D_{2d}	$^2B_1$	-4587.71000	0.003	a_2	-35	S_4	
				e	-35	C_1	$C_2(C_2')$, $C_s(\sigma_d)$
				b_1	-34	D_2	
D_2	^2A	-4587.73311	0.027	-			

$^1[dmaphPc]^0$

G	Γ_0	E_{DFT} [Hartree]	E_{JT} [eV]	Λ_{im}	ν_{im} [cm^{-1}]	K(G, Λ_{im})	E(G, Λ_{im})
D_{4h}	$^1A_{1g}$	-4587.60177	0.000	a_{2g}	-389	C_{4h}	
				e_g	-47, -30, -23	C_i	$C_{2h}(C_2')$, $C_{2h}(C_2'')$
				b_{1u}	-45	$D_{2d}(C_2')$	
				a_{1u}	-43	D_4	
				b_{2u}	-33, -24	$D_{2d}(C_2'')$	
				a_{2u}	-26	C_{4v}	
D_4	$^1A_1$	-4587.62991	0.766	a_2	-196	C_4	
				e	-25	C_1	$C_2(C_2')$, $C_2(C_2'')$
				b_2	-22	$D_2(C_2'')$	
D_{2d}	$^1A_1$	-4587.62273	0.570	a_2	-190, -36	S_4	
				e	-35	C_1	C_2, C_s
				b_1	-35	D_2	
D_2	^1A	-4587.64720	1.236	b_1	-180	C_2	
C_{4v}	$^1A_1$	-4587.60400	0.061	a_2	-331	C_4	
				e	-39, -27	C_1	$C_s(\sigma_v)$, $C_s(\sigma_d)$
				b_1	-36	$C_{2v}(\sigma_v)$	
				a_2	-35	C_4	
				b_2	-28	$C_{2v}(\sigma_d)$	
C_{2v}	$^1A_1$	-4587.62276	0.571	a_2	-190, -36, -35	C_2	
				b_1	-35	$C_s(\sigma_v)$	
				b_2	-35	$C_s(\sigma_v')$	
C_2	^1A	-4587.64969	1.304	-		-	

Table 2. Representations Γ_2 and excitation energies E_{exc} of low excited electron states in optimized $[dmaphPc]^q$ geometries of various symmetry groups.

$^1[dmaphPc]^{2-}$

D_{4h}		D_4	
Γ_2	E_{exc} [eV]	Γ_2	E_{exc} [eV]
		1^1E	1.880
		2^1E	2.155
		1^1B_1	2.160
		1^1A_1	2.234
		3^1E	2.242
		2^1B_1	2.274

$^2[dmaphPc]^{-}$

D_{4h}		D_4		D_{2d}		D_2	
Γ_2	E_{exc} [eV]	Γ_2	E_{exc} [eV]	Γ_2	E_{exc} [eV]	Γ_2	E_{exc} [eV]
		1^2B_1	0.944	1^2B_2	0.927	1^2B_1	0.917
		1^2A_2	1.232	1^2E	1.580	1^2B_3	1.548
		1^2E	1.670	2^2E	1.853	1^2B_2	1.550
		1^2B_2	1.693	2^2B_2	1.917	2^2B_3	1.797
		2^2E	1.825	3^2E	2.168	3^2B_2	1.803
		3^2E	1.848	1^2A_1	2.204	2^2B_1	1.895

$^1[dmaphPc]^0$

D_{4h}		D_4		D_{2d}		D_2	
Γ_2	E_{exc} [eV]	Γ_2	E_{exc} [eV]	Γ_2	E_{exc} [eV]	Γ_2	E_{exc} [eV]
		1^1B_1	0.847	1^1A_2	1.206	1^1B_1	1.184
		1^1B_2	0.929	1^1B_2	1.662	1^1B_2	1.483
		1^1E	0.940	1^1E	1.663	1^1B_3	1.485
		1^1A_2	0.944	1^1A_1	1.684	1^1A	1.494
		2^1A_2	1.109	2^1E	1.726	2^1B_1	1.549
		2^1E	1.392	1^1B_1	1.739	2^1B_3	1.902

C_{4v}		C_{2v}		C_2	
Γ_2	E_{exc} [eV]	Γ_2	E_{exc} [eV]	Γ_2	E_{exc} [eV]
1^1B_1	0.813	1^1A_2	1.217	1^1A	1.625
1^1A_2	1.049	1^1B_2	1.659	1^1B	1.730
1^1B_2	1.089	1^1A_1	1.662	2^1B	1.736
1^1E	1.092	1^1B_1	1.664	2^1A	1.743
1^1A_1	1.125	2^1A_1	1.676	3^1A	1.857
2^1E	1.134	2^1B_1	1.722	3^1B	2.142

CONCLUSIONS

PJT symmetry descent can proceed *via* various symmetry descent paths in multiple steps

PJT symmetry descent paths
(PJT interactions are in parentheses):

$^1[dmaphPc]^{2-}$

$D_{4h}(A_{1u}\text{-}a_{1u}) \rightarrow D_4$

$^2[dmaphPc]^{-}$

$D_{4h}(B_{1g}\text{-}b_{1u}) \rightarrow D_{2d}(A_1\text{-}b_1) \rightarrow D_2$

$D_{4h}(B_{2g}\text{-}b_{2u}) \rightarrow D_{2d}(A_1\text{-}b_1) \rightarrow D_2$

$D_{4h}(A_{1g}\text{-}a_{1u}) \rightarrow D_4(B_2\text{-}b_2) \rightarrow D_2$

$^1[dmaphPc]^0$

$D_{4h}(B_{1u}\text{-}b_{1u}) \rightarrow D_{2d}(E\text{-}e) \rightarrow C_2$

$D_{4h}(B_{1u}\text{-}b_{1u}) \rightarrow D_{2d}(B_1\text{-}b_1) \rightarrow D_2(B_1\text{-}b_1) \rightarrow C_2$

$D_{4h}(A_{1u}\text{-}a_{1u}) \rightarrow D_4(E\text{-}e) \rightarrow C_2$

$D_{4h}(A_{1u}\text{-}a_{1u}) \rightarrow D_4(B_2\text{-}b_2) \rightarrow D_2(B_1\text{-}b_1) \rightarrow C_2$

$D_{4h}(A_{2u}\text{-}a_{2u}) \rightarrow C_{4v}(B_2\text{-}b_2) \rightarrow C_{2v}(A_2\text{-}a_2) \rightarrow C_2$

TD-DFT calculations of D_{4h} symmetry structures are in progress

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