

From Conformational Properties of 4-(4-Tritylphenoxy)phthalonitrile Precursor to Conformational Properties of Substituted Phthalocyanines

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The conformational properties and structure of the conformers of 4-(4-tritylphenoxy)phthalonitrile (C₃₃H₂₂N₂O), acting as a precursor for the synthesis of tritylphenoxy substituted phthalocyanines, were investigated by DFT method. The conformational analysis of the C₃₃H₂₂N₂O molecule indicates the possibility of formation of conformers of substituted phthalocyanines with different orientations of 4-tritylphenoxy substituents, including those with a combination of cis- and trans- positions within one complex.

Keywords: Tritylphenoxyphthalonitrile, conformer, DFT, molecular structure.

От конформационных свойств прекурсора 4-(4-тримилфенокси)фталонитрила к конформационным свойствам замещенных фталоцианинов

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DFT методом исследованы конформационные свойства и строение конформеров 4-(4-тримилфенокси)фталонитрила (C₃₃H₂₂N₂O), выступающего как исходное соединение для синтеза фталоцианинов с тримилфенокси-группами в качестве периферийных заместителей. Проведенный конформационный анализ молекулы C₃₃H₂₂N₂O указывает на возможность образования конформеров замещенных фталоцианинов с разной ориентацией 4-тримилфенокси-заместителей, в том числе и с комбинацией цис- и транс-положений в пределах одного комплекса.

Ключевые слова: Тримилфеноксифталонитрил, конформер, DFT, молекулярная структура.

Among the huge amount of phthalocyanines synthesized to date, a special place is occupied by compounds containing trityl groups. Such phthalocyanines, among others, include 2(3),9(10),16(17),23(24)-tetrakis(4-tritylphenoxy)phthalocyanine and its complexes with various metals.

It is known that phthalonitriles are widely used as precursors for the synthesis of phthalocyanines and macro-

heterocyclic compounds.^[1] The presence of bulk trityl groups in phthalocyanine and its complexes determines the manifestation of mesogenic properties,^[2-4] in addition, these compounds are promising for use in thin-film electronics.^[5] The precursor for the synthesis of phthalocyanines including trityl groups is 4-(4-tritylphenoxy)phthalonitrile (TPPN).

In this paper, the conformational properties of TPPN, which can influence the structure of phthalocyanines with trityl groups, are considered.

Quantum-chemical modeling of the $C_{33}H_{22}N_2O$ molecule (Figure 1) was implemented using the Gaussian 09 program.^[6] The calculations were performed using the density functional theory (DFT) method, variants of hybrid functionals: B3LYP,^[7-9] PBE,^[10,11] CAM-B3LYP,^[12] as well as the B97D functional,^[13] which takes into account dispersion interactions. The atoms of carbon, oxygen, nitrogen, and hydrogen were described using correlation-consistent three-exponential valence bases cc-pVTZ.^[14] Geometric optimization of the structures shown in Figures 1 and 2 has been performed.

The TPPN molecule has six torsion coordinates that determine the rotation of four phenyl groups around the C-C bonds, as well as the rotation of the oxyphthalonitrile and phthalonitrile groups around the C-O bonds. Theoretical calculations performed using four functionals lead to consistent results. For identical molecular forms, the differences in the corresponding internuclear distances do

not exceed 0.002 Å, in the values of valence angles of 1°, and less than 7° in the values of torsion angles. All variants of the DFT method predict the presence of four C_1 symmetry conformers for the $C_{33}H_{22}N_2O$ molecule (Figure 1).

It should be noted the general structural motives of conformers. Thus, the central site C(C)₄ of the (Ph)₃C(PhO) fragment is a distorted tetrahedron with identical C-C bonds, two C-C-C bond angles that are smaller than tetrahedral one, and four C-C-C bond angles larger than tetrahedral one (Table 1). In all conformers, the plane of the PhO fragment is located almost perpendicular to the plane of the phthalonitrile fragment (PhN), as is the plane of one of the phenyl fragments of the trityl group C(Ph)₃ (Figure 1). *Cis*-conformers **I** and **II** differ from *trans*-conformers **III** and **IV** in the value of the torsion angle ($\approx 0^\circ$ and $\approx 180^\circ$), which determines the rotation of the (Ph)₃C(PhO) fragment around the O-C_{PhN} bond. The difference in the two *cis*-conformers **I** and **II**, as well as in the two *trans*-conformers **III** and **IV**, lies in the different relative orientation of the three phenyl fragments in the trityl group (Figure 1).

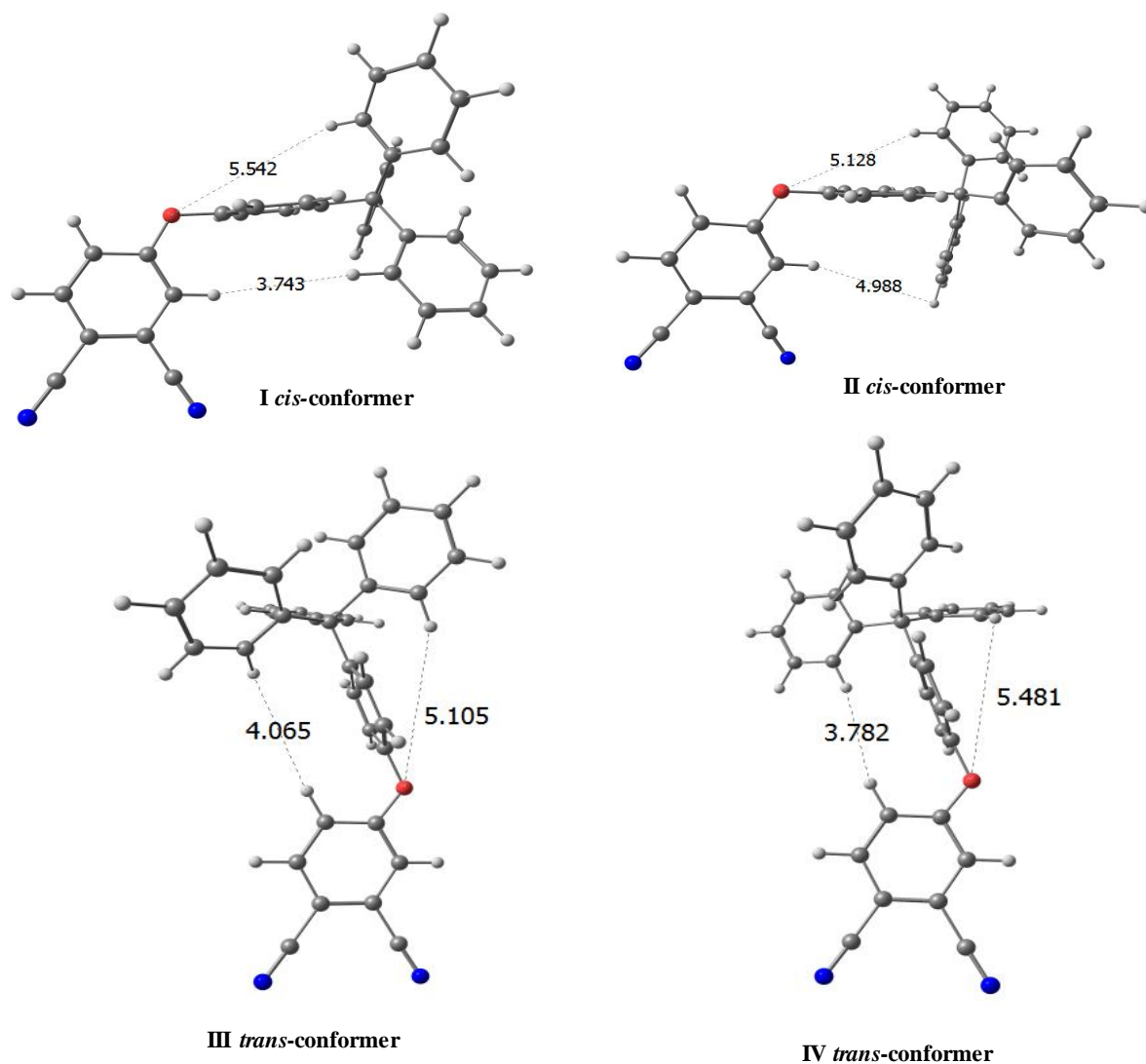


Figure 1. Geometric structures of *cis*- and *trans*-conformers of the 4-(4-tritylphenoxy)phthalonitrile molecule.

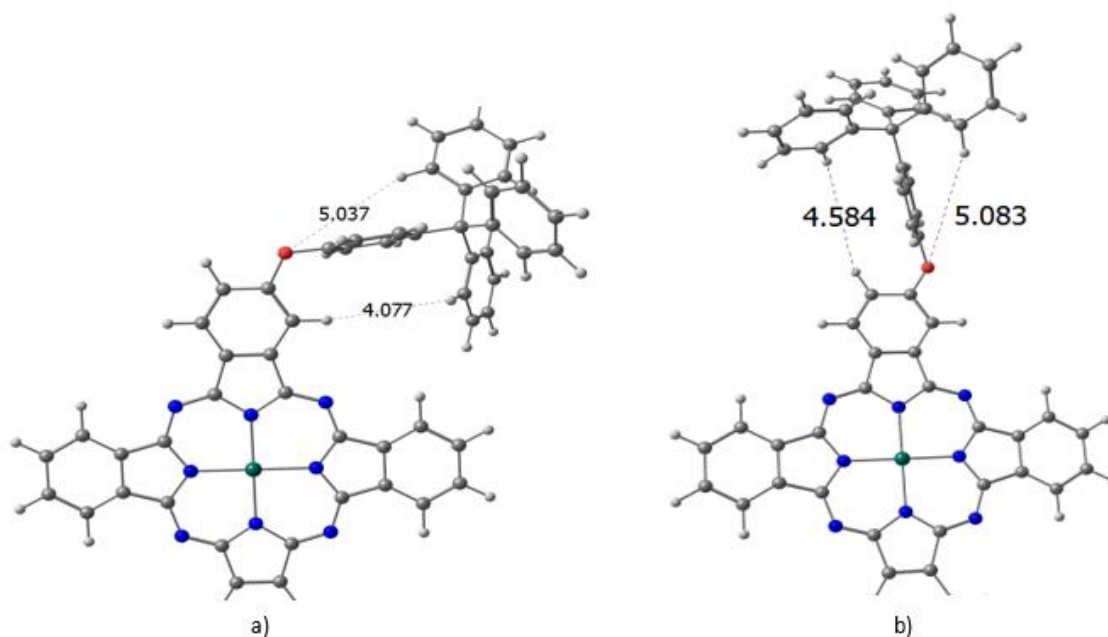


Figure 2. Structure of zinc phthalocyanine with different orientation of the 4-tritylphenoxy substituent.

Table 1. Selected characteristics of conformers of $C_{33}H_{22}N_2O$ molecule according to DFT/B3LYP/cc-pVTZ¹.

	Conformer			
	I	II	III	IV
ΔE_{total} , kcal/mol	0.105	0	0.337	0.272
E_{HOMO} , eV	-6.75	-6.76	-6.86	-6.83
E_{LUMO} , eV	-2.38	-2.36	-2.31	-2.33
μ , D	8.18	8.10	10.05	9.97
Parameters of a distorted tetrahedron (CC ₄) built from carbon atoms of four phenyl fragments				
C-C (CC ₄) ^a , deg.	1.554	1.554	1.555	1.554
C-C-C _{av} (4) ^b , deg.	111.6	111.7	111.4	111.7
C-C-C _{av} (2) ^c , deg.	105.3	104.9	105.8	105.1
Parameters of Ph-O-PhN moiety				
C _{Ph} -O, Å	1.396	1.396	1.395	1.395
O-C _{PhN} , Å	1.358	1.358	1.358	1.359
C≡N, Å	1.152	1.152	1.152	1.152
C-O-C, deg.	120.3	120.2	120.4	120.3

^aaveraged; ^baveraged value of four angles; ^caveraged value of two angles.

All conformers have close energies of boundary orbitals and large dipole moments (Table 1), however, the direction of dipole moments in *cis*-conformers differs significantly from their direction in *trans*-conformers.

Despite the significant difference in structure, the conformers have close electronic energies, which increases the probability that the TPPN substance may contain

different conformations in the unit crystal cell or have a complex conformational composition of the gas phase.

The relative Gibbs free energies and conformational equilibrium constants were calculated for the *cis*- and *trans*-conformers free of intermolecular interaction. It is shown that the ratio between the molar fractions of the *cis*- and *trans*-conformers is close to 1.

The conformational diversity of TPPN, which is the precursor for the synthesis, can be the reason for the different geometry of phthalocyanines containing trityl groups in their composition. Figure 2 shows two calculated structures of the zinc phthalocyanine complex, differing in the position of the 4-tritylphenoxy substituent.

As can be seen from Figures 1 and 2, the structure (2a) has a substituent orientation similar to the orientation of the 4-tritylphenoxy group in *cis*-conformers I and II of TPPN, and the structure (2b) has a substituent orientation similar to that in *trans*-conformers III and IV. The models (2a and 2b) differ in energy only by 0.011 kcal/mol and do not have significant steric hindrance (the shortest distances between substituents and the macroheterocycle exceed 4 Å).

Thus, the conformational analysis performed for the 4-(4-tritylphenoxy)phthalonitrile molecule, as a precursor, indicates the possibility of formation of conformers of substituted phthalocyanines with different orientations of 4-tritylphenoxy substituents, including those with a combination of *cis*- and *trans*-positions within one complex.

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