

Conformational analysis and nonlinear optical properties of the N, N'-pentamethylenebis(salicylideneiminato)manganese(II) complex

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Conformational analysis of the tricyclic Schiff base chelate complex N,N'-pentamethylenebis(salicylideneiminato)manganese(II) is performed by means of the molecular mechanic (MM⁺), semi-empirical PM3 and density functional (B3LYP/LanL2DZ) methods, respectively. Eight starting structures of the complex are minimized. The structures of the three lowest minimum energy conformations of cyclooctane, boat-chair (*bc*), chair-chair (*cc*) and boat-boat (*bb*), are used as initial approximations to the geometry of the eight-membered chelate ring. The absolute-MEC (Mn-*bc4*) and the most unstable one (Mn-*bb*) originate from the boat-chair-shaped form of the eight-membered cycle, differing in the position of the metal atom. After the conformational analysis of the tricyclic Schiff base chelate complex, nonlinear optical properties and optical band gap ($E_{HOMO-LUMO}$) were calculated with B3LYP/LanL2DZ level of theory for all conformations. The frontier molecular orbital calculations clearly show the inverse relationship of optical band gap ($E_{HOMO-LUMO}$) with the total static hyperpolarizability.

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1. Introduction

Manganese-containing enzymes play an important role in the oxygen metabolism [1], and in particular in photosynthesis [2,3]. Numerous synthetic high-oxidation-state manganese complexes with Schiff base ligands and their Mn(II) precursors have attracted considerable interest as oxygen-carrier biomimetic models [4-7]. A large series of Mn(II) complex with tetradentate ligands derived from salicylaldehyde and α,ω -diaminoalkanes have been synthesized and have been shown to react with dioxygen forming Mn(III) or Mn(IV) species. The structure of these complexes has been subjected a discussion since they may exist as monomeric, oligomeric or polymeric species, containing tetrahedrally coordinated Mn(II) [4]. The monomeric species should contain a tricyclic chelate system which is expectable to exhibit interesting conformational behaviour, especially when the aliphatic chain between the two donor nitrogen atoms is enough long.

The molecular mechanics and semi-empirical methods, being less time consuming as compared to the ab-initio methods are widely used tools of the theoretical conformational analysis and give reliable results when applied to organic molecules [8]. MM and semi-empirical calculations of inorganic and bioinorganic systems have been intensively studied in early stage calculations [7,9-10].

Nonlinear optical properties of a variety of systems, such as organic and anorganic molecules, metal and transition metal systems were studied by different

approaches. Although organic molecular systems have been extensively studied by both semi-empirical and ab-initio methods, organometallic systems have received less attention due to the difficulty in calculation hyperpolarizabilities in the presence of transition metal atoms. Semi-empirical methods have been less reliable for to calculate nonlinear optical properties (NLO) of organometallic systems due to parameterisation problems [11]. ZINDO-SOS and restricted Hartree-Fock (RHF) methods were used by numerous researchers for calculating second order molecular optical nonlinearities of organometallic systems [12-17].

Due to high accuracy results, density functional theory (DFT) has become a popular alternative to traditional ab-initio methods in calculating nonlinear optical properties. However, the application of DFT theories for calculation of polarizabilities of organometallic complexes has been limited due to the large computational cost. The DFT results with extended basis sets are more reliable than the Hartree-Fock calculations with comparable basis sets [11] due to the incorporate correlation effect into the model Hamiltonian, whereas in standard restricted Hartree-Fock methods correlation effects must be specifically added [18].

In the present study, the MM⁺, PM3 and density functional (B3LYP) methods are applied to obtain information about the shape and relative energies of the most stable conformers the monomeric form of [N,N'-pentamethylenebis(salicylideneiminato)-N,N',O,O']manganese(II) (Mn-pmsal) (Fig. 1) previously reported by Titus *et al.* [4]. After the conformational

analysis of the tricyclic Schiff base chelate complex, our second aim is to calculate nonlinear optical properties such as static polarizability, first static hyperpolarizability and optical band gap ($E_{HOMO-LUMO}$) with B3LYP/LanL2DZ level of theory for all conformations.

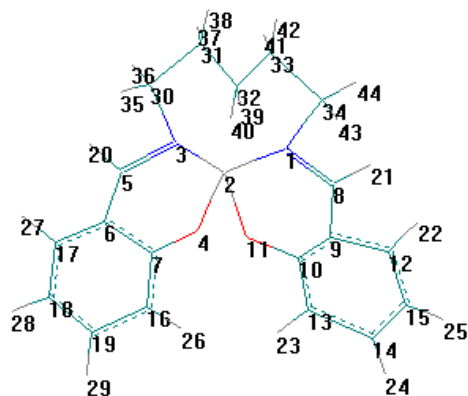


Fig. 1. Structural formula of Mn-pmsal with the atom labeling scheme used herein. In this figure, 3 and 1, 4 and 11, and 2 represent nitrogen, oxygen and manganese atoms, respectively.

2. Computational

Conformational analysis of Mn-pmsal has been studied using molecular mechanic (MM), semi-empirical PM3 and density functional (B3LYP/LanL2DZ) methods, respectively. MM and PM3 calculations were performed with the HYPERCHEM 7.0 programme, MM+ parameter set is utilized for MM method, based on the Allinger's MM2 force field [19]. The total energy was used as a measure of the relative stability of the conformations.

The accuracy and reliability of DFT/B3LYP functional was shown in computing various molecular properties such as nonlinear optical properties, HOMO-LUMO energies etc. of organic and organometallic systems [11, 20-22]. For these reasons optical band gap ($E_{HOMO-LUMO}$) and nonlinear optical properties of all conformations were calculated with DFT method at B3LYP/LanL2DZ [23-25] level of theory using the Gaussian 03W software [26].

3. Results and discussion

An important starting point of each conformational calculation is the choice of the initial approximations of the structure to be optimised in order to find the different conformations corresponding to minima on the energy surface in the space of the internal coordinates. The most flexible part of the Mn-pmsal molecule is the eight-membered chelate ring, so the geometry of the minimum energy conformations (MEC) of cyclooctane ring can be used as initial approximations to its geometry. Anet and Krane [27] have found eight MEC of cyclooctane molecule by means of MM calculations. Rocha *et al.* [28] was comprehensively investigated the potential energy surface (PES) of cyclooctane molecule at the Hartree-Fock(HF) level of theory employing the 3-21G, 6-31G, and 6-31G* basis sets. They found six distinct true minimum energy structures characterized by harmonic frequency analysis which were located on the multidimensional PES. Two transition state structures were also located on the PES for the cyclooctane molecule. The global minimum energy structure on the PES for cyclooctane molecule was predicted as *bc* conformer. The absolute-MEC and the next two MEC in energy are depicted in Fig. 2.

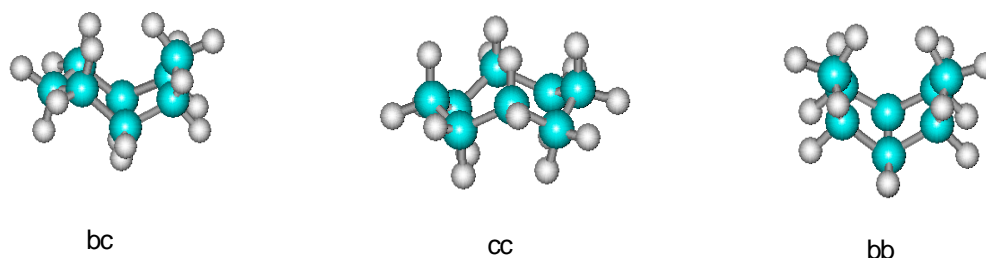


Fig. 2. Three of the lowest minimum-energy conformations of cyclooctane: boat-chair (*bc*), chair-chair (*cc*) and boat-boat (*bb*)

We have restricted our consideration to these three conformations only. Energy values of *bc*, *cc* and *bb*

conformations of cyclooctane with their HOMO-LUMO energy are given in Table 1.

Table 1. Energy values of the conformations of cyclooctane

Conformations	Total Energy (kJ/mol)			Energy of molecular orbitals with B3LYP/LanL2DZ method (eV)	
	MM	PM3	B3LYP/LanL2DZ	HOMO	LUMO
bc	78	-39057.20	-825945.68	-7.50	-2.67
cc	81	-38988.07	-825942.02	-7.54	-2.72
bb	96	-38985.85	-825931.69	-7.48	-3.06

Due to symmetry reasons, five initial structures originating from the absolute-MEC of cyclooctane have to be regarded, corresponding to the five non-equivalent positions which Mn and the two N-donor atoms can occupy on the *bc*-shaped ring. Further, two and one such structures are possible for *bb* and *cc* ring, respectively.

The absolute-MEC (Mn-*bc4*) and the most unstable one (Mn-*bb*) originate from the *boat-chair*-shaped form of the eight-membered cycle, differing in the position of the metal atom. In all the MEC the coordination, polyhedron

of Mn(II) is a distorted tetrahedron. As can be seen from Table 2, the lowest energy conformation, Mn-*bc4*, is characterised by the greatest deviations of the Mn-atom bond angle from the ideal tetrahedral value, whereas for Mn-*bc* and the most unstable MEC, Mn-*bb*, these deviations are smaller. For the latter conformation, the couple of bonds N₁-Mn and N₃-C₃₀ are in almost eclipsed orientation, and this distortion also contributes the energy of Mn-*bb* to be much higher with respect to all the remaining MEC.

Table 2. Bond angles for different conformations of Mn-pmsal complex

Conformations	O ₄ MnN ₃	O ₄ MnN ₁	O ₄ MnO ₁₁	O ₄ MnN ₃	O ₁₁ MnN ₁	N ₃ MnN ₁	C ₃₁ C ₃₀ N ₃ C ₅
Mn(bc1)	98	120	116	118	99	105	-86
Mn(bc2)	98	111	121	119	99	109	-78
Mn(bc3)	95	94	101	135	93	128	172
Mn(bc4)	98	109	121	116	99	113	-155
Mn(bc5)	99	116	125	107	98	111	116
Mn(cc)	98	109	121	116	99	113	-155
Mn(bb)	98	112	124	112	98	115	-165

The structure of the lowest-energy conformation of Mn-pmsal is drawn in Fig. 3. The benzene ring carbons together with the corresponding C, N, Mn and O atoms remain nearly coplanar, preserving the π -electron-conjugated character of these fragments. For the highest-energy MEC, however, more considerable deviation of the six-membered chelate rings from planarity take place, *e. g.* the torsional angles C₆C₇O₄Mn₂ and C₇O₄Mn₂N₃ are 21 and 25°, respectively.

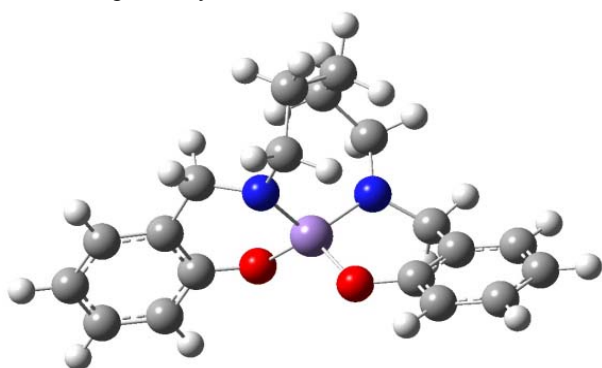


Fig. 3. Structure of minimum-energy conformation of Mn-pmsal complex

3.1 Frontier molecular orbital analysis

The calculations indicate that the absolute-MEC (Mn-*bc4*) has 91 occupied and unoccupied molecular orbitals (MO). The optical band gaps for all conformations were calculated and are presented in Table 3.

The 3D plots of important molecular orbitals are shown in Fig. 4 for Mn-*bc4*. The frontier molecular orbitals play an important role in the electronic and optical properties, as well as in UV-vis spectra and chemical reactions [29]. Also, the energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties and an electronic system with a larger HOMO-LUMO gap should be less reactive than with a smaller gap [30]. The energy gap of HOMO-LUMO explains the eventual charge transfer interaction within the molecule. In this study, the frontier orbital energy gap in case of MEC conformations of Mn-pmsal, Mn-*bc4*, is found to be 2.47 eV by B3LYP method with LanL2DZ basis set.

Table 3. Total energies, energy differences (kcal/mol) and optical band gaps ($\Delta E_{HOMO-LUMO}$) for true minimum energy structures on potential energy surface for Mn-pmsal.

Conformations	E(kcal/mol)	ΔE (kcal/mol)	$\Delta E_{HOMO-LUMO}$ (eV)
Mn(bc1)	-690900.12	4.24	2.96
Mn(bc2)	-690899.95	4.41	2.47
Mn(bc3)	-690897.64	6.72	2.25
Mn(bc4)	-690904.36	0	2.47
Mn(bc5)	-690903.90	0.46	2.37
Mn(cc)	-690903.50	0.86	2.29
Mn(bb)	-690896.43	7.93	3.04

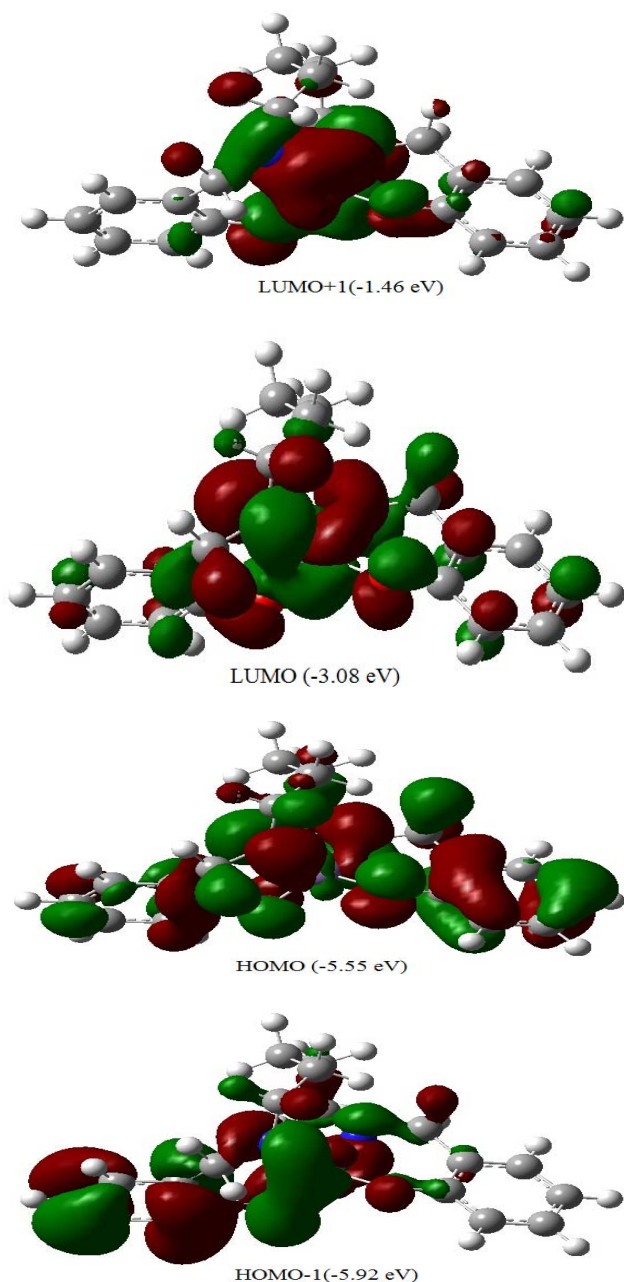


Fig. 4. Molecular orbital electron density of Mn-pmsal complex

3.2 Nonlinear optical properties

The search of new materials exhibiting efficient nonlinear optical properties has been of great interest in recent years because of their potential applications in optoelectronic devices of telecommunications, information storage, optical switching, signal processing [31-35] and terahertz (THz) wave generation [36]. The synthesis of various transition metal complexes as potential NLO materials for frequency doubling and optical electrical modulators has attracted increasing attention [37-40]. Organometallic and coordination complexes are interesting candidates for NLO purposes [11].

It is well known that the nonlinear optical response of an isolated molecule in an electric field E_i can be presented as a Taylor series expansion of the total dipole moment, μ_{tot} , induced by the field:

$$\mu_{tot} = \mu_0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \dots$$

Where α is the linear polarizability, μ_0 the permanent dipole moment and β is the first hyperpolarizability tensor components. The isotropic (or average) linear polarizability and anisotropy of polarizability, respectively, are defined as [41]:

$$\langle \alpha \rangle = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\Delta \alpha = 1/2^{1/2} [(\alpha_{xx} - \alpha_{yy})^2 + [(\alpha_{xx} - \alpha_{zz})^2 + [(\alpha_{yy} - \alpha_{zz})^2]^{1/2}]^{1/2}$$

The complete equation for calculating the total static first hyperpolarizability magnitude of Gaussian output is given as follows [42],

$$\beta_{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

Static mean polarizability ($\langle \alpha \rangle$), anisotropy of polarizability ($\Delta \alpha$) and first static hyperpolarizability β_{tot} are listed in the Table 4. Nonlinear optical activity is characterized by hyperpolarizability. As can be seen from Table 4, the largest hyperpolarizabilities were obtained for Mn-bc3 and Mn-cc conformations. Also as can be seen from Table 3 and Table 4, there is an inverse relationship between optical band gap ($E_{HOMO-LUMO}$) and first static hyperpolarizability (β) [42].

Table 4. Static average polarizability ($\langle\alpha\rangle$), anisotropy of polarizability ($\Delta\alpha$) and first static hyperpolarizability (β) at the B3LYP/LanL2DZ level of theory for different conformations of Mn-pmsal complex

Conformations	$\langle\alpha\rangle/\text{a.u.}$	$\Delta\alpha/\text{a.u.}$	$\beta_{\text{tot}}/\text{a.u.}$
Mn(bc1)	273.04	141.05	1043.05
Mn(bc2)	289.03	155.15	2158.02
Mn(bc3)	267.66	103.94	2659.55
Mn(bc4)	287.68	149.68	2133.43
Mn(bc5)	289.43	160.06	2285.39
Mn(cc)	296.99	165.90	2693.23
Mn(bb)	272.65	103.90	1420.65

4. Conclusions

We have investigated the conformational analysis and nonlinear optical properties of the title compound. The following conclusions can be drawn from the theoretical studies:

The conformational behaviour Mn-pmsal, containing one eight-membered and two six-membered chelate rings, was studied by the molecular mechanics (MM⁺), semi-empirical PM3 and density functional (B3LYP/LanL2DZ) methods, respectively. Starting from eight different structures derived from the *boat-chair*, *chair-chair* and *boat-boat* conformations of the eight-membered cycle, seven minimum energy conformations of the complex molecule were obtained.

Five of these MEC (among them the lowest-energy conformation) were derived from *bc*-shaped structure of the eight-membered ring, one was its *cc* conformation, and the others were form *bb* conformation.

Mn(II) is in a distorted tetrahedral surrounded of the N- and O-donor atoms, in all the conformations.

In all the MECs, except the highest energy one, the benzene ring and the six-membered chelate ring, are nearly coplanar.

The inter conversion of the conformers seems to be easily realizable at ambient temperature.

According to the calculated β values, it is clear that the NLO responses are larger for Mn-bc3 and Mn-cc conformations than other conformations, and these structures present large nonlinear optical activity.

The HOMO–LUMO calculations show that the first hyperpolarizability of these conformations is directly related to the ($E_{\text{HOMO-LUMO}}$) optical band gap with an inverse relationship between two properties.

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