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A Combined Theoretical Investigation and X-Ray Study of 2-(4-Dimethylamino)benzylideneamino)-3-aminomaleonitrile

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Abstract

In the present work a Schiff base ligand 2-(4-(dimethylamino)benzylideneamino)-3-aminomaleonitrile was prepared via condensation of diaminomaleonitrile and 4-(dimethylamino)benzaldehyde under reflux. This compound was characterized by elemental analysis, FT-IR spectroscopy and single crystal X-ray diffraction. The ground state properties of the title molecule have been calculated employing DFT/B3LYP level of the theory using the 6-31G (d, p) basis set. The first static hyperpolarizability of this compound is found to be 26.76×10^{-30} (esu). So this imino compound is a suitable molecule for optical nonlinearity. Calculated bond lengths and bond angles are in good agreement with X-ray data.

Keywords: DFT/B3LYP, 6-31G (d, p), hyperpolarizability, nonlinear optical property (NLO), theoretical study

Introduction

Hugo Schiff described the condensation between an aldehyde and an amine leading to a Schiff base in 1864 [1]. Schiff base ligands are able to coordinate metals through the imine nitrogen and another groups, usually linked to the aldehyde. Schiff base ligands are one the oldest classes of ligands in coordination chemistry and these compounds have been used extensively for coordination with transition and main group metal ions [2]. Also Schiff base compounds have been studied in the area of bioinorganic chemistry where interest in Schiff bases complexes with transition and inner-transition metals has centered on the role of such complexes in providing synthetically interesting models for the metal-containing sites in metallo-proteins and enzymes [3-9], whereas, unsymmetrical Schiff bases ligands have clearly offer many advantages over their symmetrical counterparts in the elucidation of the composition and geometry of the metal ion binding sites in the metallo-proteins and -enzymes, and selectivity of natural systems with synthetic materials. Recent years have witnessed a great deal of interest in the synthesis and characterization of transition metals complexes containing Schiff bases as ligands due to their applications as catalysts for many reactions [10-14] and relation to synthetic and natural oxygen carriers. On the other hand considerable interest has been shown in the preparation of compounds with nonlinear optical properties (NLO), which find application in dye laser technology and optical devices [17,18]. Furthermore, quantum chemistry calculations have proved to be useful in the description of the relationship between the electronic structure of molecular system and its non-linear optical response [15-

18]. However, in this new study, the 2-(4-(dimethylamino)benzylideneamino)-3-aminomaleonitrile was synthesized and some calculations regarding the hyperpolarizability, dipole moment, bond length, bond angle, molecular orbital levels, the first hyperpolarizability (β) and charge density on all atoms in its structure were evaluated. The β value obtained from the theoretical calculations are compared with those for a standard choromophore, *p*-nitro aniline (PNA), ($\beta = 34.5\times10^{-30}$ esu) [19,20]. The values usually calculated are the molecular quantities: a, b, and g, which are polarizability, first-order hyperpolarizability, and the second-order hyperpolarizability tensors, respectively. A value that is useful in measuring second-order NLO properties is the mean first-order hyperpolarizability, which is calculated as shown in this equation,

$\beta = \beta_{ZXX}+\beta_{ZYY}+\beta_{ZZZ}$.

Experimental section

All the chemical reagents were purchased from Merck Company and used as received. The ligand 2-(4-(dimethylamino)benzylideneamino)-3-aminomaleonitrile (whose structure is shown in **Figure 1**) was synthesized by condensation of a methanolic solution of diaminomaleonitrile and a methanolic solution of 4-(dimethylamino)benzaldehyde (molar ratio 1:1) under reflux for 2 h. Small light-red crystals were filtered and recrystallized from acetonitrile. The prepared Schiff base ligand 2-(4-(dimethylamino)benzylideneamino)-3-aminomaleonitrile was characterized by satisfactory microanalyses, FTIR and X-ray crystallography. C, H and N microanalyses were accomplished on a Perkin Elmer analyzer with KBr disk and FTIR spectra was measured on a Shimadzu DR-8001 spectrometer. The IR spectra of this compound confirm the presence of an imine bond (C=N) at 1635 cm^{-1}, the C=C vibrational band of aromatic ring at 1473 cm^{-1}, the (N-H) band at 3398-3485 cm^{-1} and the nitrile bond (C≡N) at 2250 cm^{-1}. The microanalyses (%) calculated (found) for $C_{13}H_{13}N_5$: C, 65.271(65.26); H, 5.439(5.39); N, 29.288(29.01). Also the X-ray single crystal data of this compound are listed in **Table 1**.

Computational details

In the present study the density functional theory DFT [21] has been employed using a B3LYP functional and a 6-31G (d, p) basis set [22]. The geometry was optimized at the B3LYP/6-31G (d, p) level for investigation of the electronic structural properties of this molecule, and to calculate the properties of this molecule, such as total dipole moment, all bond lengths and bond angles, polarizability, heat of formation and binding energy, highest occupied molecular level (HOMO), and lowest unoccupied molecular orbital level (LUMO). All the calculations were carried out with the GAUSSIAN 03 software [23].

Results and discussion

In summary, the synthesis of 2-(4-(dimethylamino)benzylideneamino)-3-aminomaleonitrile compound and X-ray crystallographic data were described. The x-ray crystallographic data of this compound are shown in **Tables 1 - 2**. All spectroscopic data for this ligand are in good accordance with X-ray crystallographic data. Some experimental selected bond lengths and bond angles are shown in **Table 2** in comparison with the calculated values at the B3LYP level. As shown in **Table 2**, the calculated bond lengths and bond angles are in agreement with crystallographic data. The molecule is optimized in gas phase and the minimum energy of 2-(4-(dimethylamino)benzylideneamino)-3-aminomaleonitrile was determined and the most stable geometry is shown in **Figure 2**, with the X-ray structure for this compound shown in **Figure 3** and its packing in **Figure 4**.

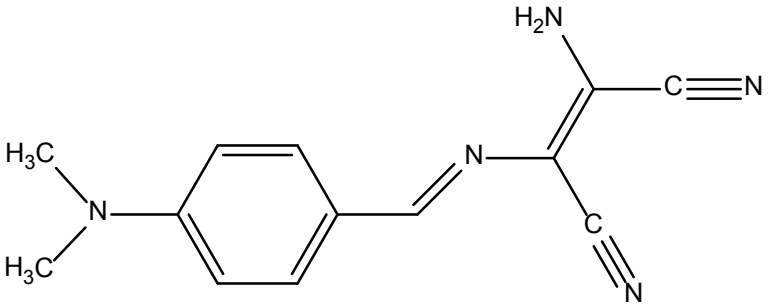

Figure 1 The structure of 2-(4-(dimethylamino)benzylideneamino)-3-aminomaleonitrile.

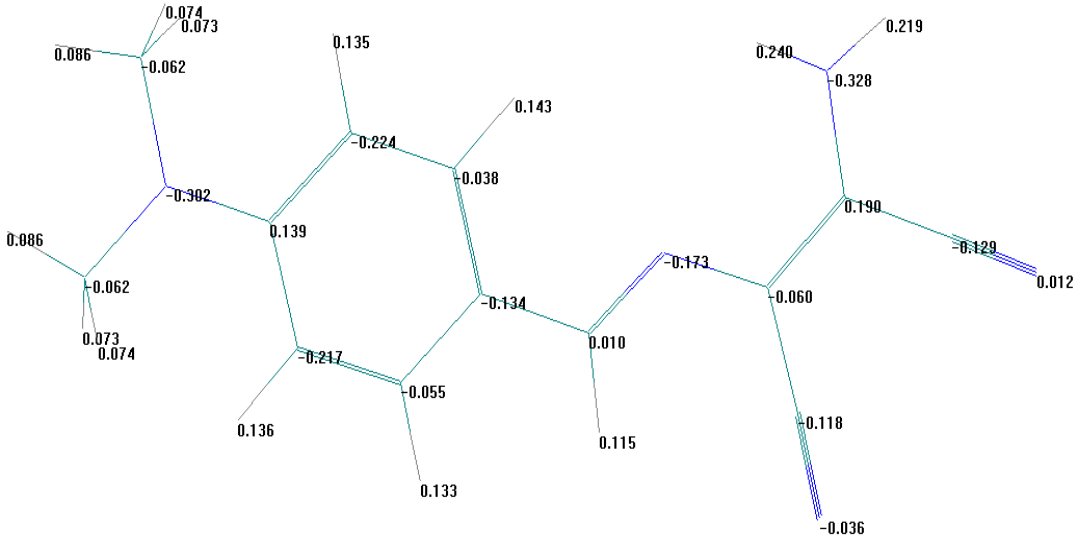

Figure 2 The optimized structure of 2-(4-(dimethylamino)benzylideneamino)-3-aminomaleonitrile compound (the calculated charge density for all atoms are shown in this structure).

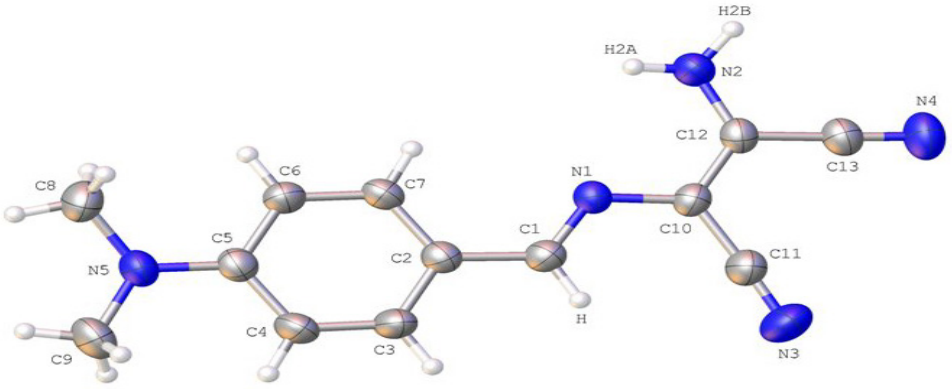

Figure 3 The X-ray structure of 2-(4-(dimethylamino)benzylideneamino)-3-aminomaleonitrile.

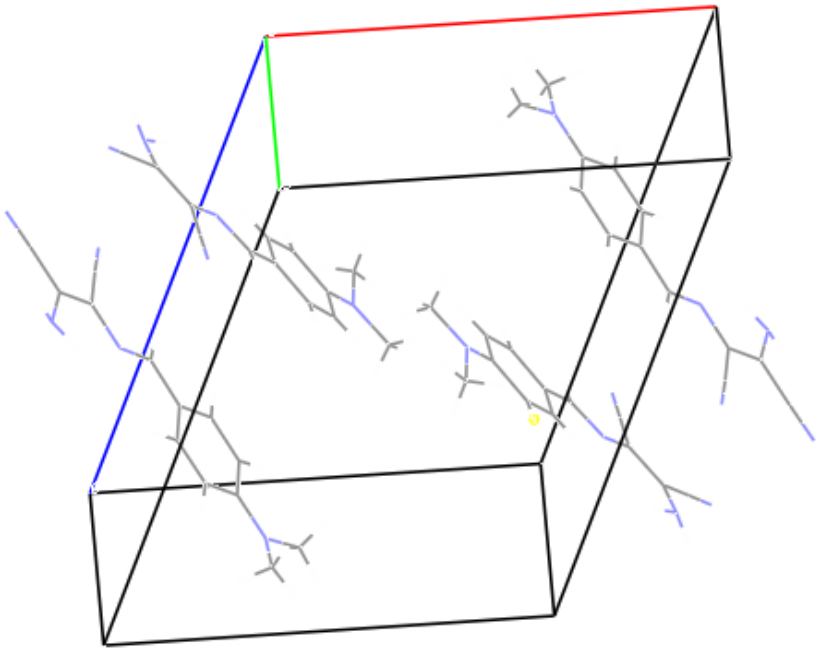

Figure 4 View of the packing for 2-(4-(dimethylamino)benzylideneamino)-3-aminomaleonitrile.

Crystallographic data of this compound are listed in **Table 1**. Energies of HOMO level and LUMO level are shown in **Figure 5**. Selected geometric parameters (bond lengths in Å, bond angles in °) and some of calculated parameters are shown in **Table 2**.

Table 1 Crystal data and structure refinement for 2-(4-(dimethylamino)benzylideneamino)-3-aminomaleonitrile.

Empirical formula	$C_{13}H_{13}N_5$
Formula weight	239.28
Space group	$P2_{1/c}$
Temperature	293(2) K
Wavelength	0.71073 A
Unit cell dimensions	a = 12.046(11) Å $\alpha = 90^o$
	b = 7.0809(5) Å $\beta = 110.92^o$
	c = 15.4653(11) Å $\gamma = 90^o$
Volume	1238.07 $Å^3$
Z, Calculated density	4, 1.249 mg/m^3
Absorption coefficient	0.080 mm^{-1}
F(000)	504
Theta range for data collection	2.70 to 25.53°
Limiting indices	14 <= h <= 14, –8 <= k <=8, –18 <= l <=19
Reflections collected / unique	16322 / 2376 [R(int) = 0.0752]
Completeness (θ = 25.53)	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2376 / 0 / 171
Goodness-of-fit on F^2	1.039
Final R indices [I > 2sigma (I)]	R1 = 0.0392, wR2 = 0.1038
R indices (all data)	R1 = 0.0557, wR2 = 0.1114
Largest diff. peak and hole	0.144 and –0.161 $e.A^{-3}$

Table 2 Selected bond lengths (Å), bond angles (°), some calculated structural parameters for 2-(4-(dimethylamino)benzylideneamino)-3-aminomaleonitrile calculated by DFT/B3LYP.

Selected bond	**Calculated bond length (Å) by DFT/B3LYP level**	**Measured bond length (Å) by X-ray**
N(2)-C(12)	1.373	1.353
C(12)-C(10)	1.390	1.361
N(1)-C(10)	1.397	1.384
N(1)-C(1)	1.295	1.279
C(1)-C(2)	1.461	1.441
C(2)-C(7)	1.401	1.393
C(3)-C(3)	1.401	1.390
N(5)-C(5)	1.389	1.372
N(5)-C(8)	1.443	1.443
N(5)-C(9)	1.431	1.447
Selected angle	**Calculated angle (°) by DFT/B3LYP level**	**Measured angle (°) by X-ray**
N(1)-C(10)-C(12)	119.85	118.20
N(1)-C(1)-C(2)	121.37	123.90
N(2)-C(12)-C(10)	123.91	124.11
N(2)-C(12)-C(13)	124.82	116.40
C(10)-C(12)-C(13)	117.96	119.40
C(3)_C(2)-C(1)	119.96	119.59

C(7)_C(2)-C(1)	121.59	12.15
N(1)-C(10)-C(11)	121.89	122.04

Parameters	**Calculation by DFT/B3LYP level**	
Heat of Formation	–133.6921864 (kcal/mol)	-
Binding Energy	–3330.2038136 (kcal/mol)	-
Molecular point group	C1	
HOMO((eV), level, 45)	–8.044	-
LUMO(eV), level, 46)	–0.945	-
Band gap(eV)	7.099	-
Dipole moment(μ) debye	$\mu_x = 6.97685$ $\mu_y = -1.988$ $\mu_z = -0.6595$ $\mu_t = 7.0935$	-
Hyperpolarizability (β)	26.76×10^{-30} (esu)	-

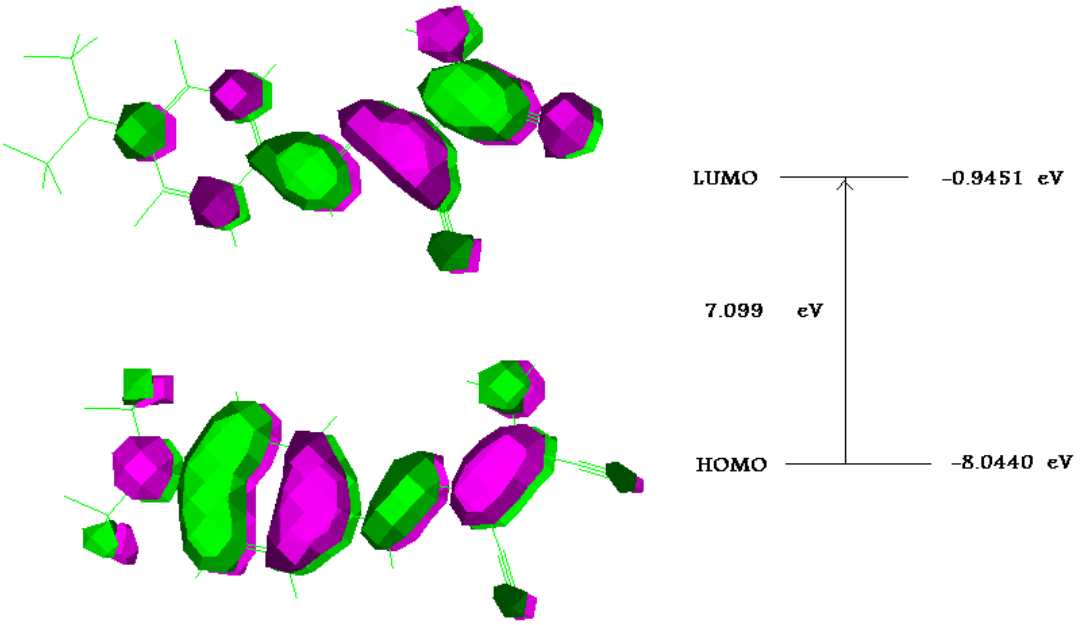

Figure 5 Theoretical calculated HOMO and LUMO molecular orbitals by DFT/B3LYP for 2-(4-(dimethylamino)benzylideneamino)-3-aminomaleonitrile.

Figure 5 shows the HOMO and LUMO for 2-(4-dimethylamino)benzylideneamino)-3-aminomaleonitrile. As is seen in **Figure 5**, the HOMO of the title compound is delocalized approximately on all atoms of this ligand. It was found that the band gap is wide; therefore, this compound can be expected to be very sensitive to laser shock. Mulliken population study shows nitrogen atom in imine group and nitrogen atom in amine group are probable coordination sites for this ligand. In the optimized structure N(1), N(5) and N(2) atoms have more negative charge density (–0.173, –0.302 and –0.328)

(**Figure 2**) than the other atoms in the structure of this compound, so these atoms are the coordination sites for the 2-(4-dimethylamino)benzylideneamino)-3-aminomaleonitrile ligand in binding to transition metal ions. **Table 2** shows the calculated bond lengths and bond angles are in good agreement with the experimental X-ray data.

Conclusions

In this study we have designed and synthesized a Schiff base ligand 2-(4-dimethylamino)benzylideneamino)-3-aminomaleonitrile with NLO properties. Its structure was characterized by common spectroscopic methods and X-ray crystallography. The first molecular hyperpolarizability(β) of this compound has been calculated by DFT theoretical method. The geometry optimization and the structural electronic properties of this compound have been carried out by using GUSSIAN 03 software. The analysis of the electronic properties was based on atomic electronic charges, electric dipole moment and polarizability tensor elements. This Schiff base compound is a suitable molecule for optical nonlinearity and the calculated bond lengths and bond angles are in good agreement with X-ray data.

References

[1] H Schiff. Mittheilungen Aus Dem Universitat Slaboratorium in Pisa: Eine Neue Reihe Organischer Basen. *Justus Liebigs. Ann. Chem.* 1864; **131**, 118-9.
[2] DN Dhar and CL Taploo. Schiff bases and their applications. *J. Sci. Ind. Res.* 1982; **41**, 501-6.
[3] PK Sasmal, S Saha, R Majumdar, RR Dighe and AR Chakravarty. Oxovanadium(IV)-Based Near-IR PDT agents: design to biological evaluation. *Chem. Commun.* 2009; **13**, 1703-5.
[4] M Roy, T Bhowmick, R Santhanagopal, S Ramakumar and AR Chakravarty. Photo-induced double-strand DNA and site-specific protein cleavage activity of L-histidine (m-oxo)Diiron(III) complexes of heterocyclic bases. *Dalton Trans.* 2009; **24**, 4671-82.
[5] MSA Begum, S Saha, M Nethaji and AR Chakravarty. Iron(III) Schiff base complexes activity. *J. Inorg. Biochem.* 2010; **104**, 477-84.
[6] CN Bhardwaj and VR Singh. Synthesis and characterization of Thallium(I) complexes of biologically active benzothiazolines. *Indian J. Chem*. 1994; **33A**, 423-5.
[7] TD Bharamagouclar, MA Pujar and AR Alagawadi. Biological activity of Schiff base and their metal complexes. *Curr. Sci.* 1987; **56**, 889-90.
[8] MD Deshmukh and AG Doshi. Synthesis of Schiff bases and their applications. *Orient. J. Chem*. 1995; **11**, 86-96.
[9] M Tumer, H Koksal, S Serin and M Digrak. Antimicrobial study of mononuclear and binuclear mixed ligand Cu (II) complexes, derived from 1, 10-phenanthroline. *Trans. Met. Chem*. 1999; **24**, 13-7.
[10] I Sheikhshoaie, A Rezaeifard, N Monadi and S Kaafi. A novel tridentate Schiff base dioxo-molybdenum(VI) complex: Synthesis, crystal structure and catalytic performance in green oxidation of sulfides by urea hydrogen peroxide. *Polyhedron* 2009; **28**, 733-8.
[11] M Hatefi, M Moghadam, V Mirkhani and I Sheikhshoaei. Silica supported Ru(salophen)Cl: An efficient and robust heterogeneous catalyst for epoxidation of alkenes with sodium periodate. *Polyhedron* 2010; **29**, 2953-8.
[12] A Nishinaga, T Yamada, H Fujisawa and K Ishizaki. Catalysis by cobalt Schiff base complexes in the oxygenation of alkenes on the mechanism of ketonization. *J. Mol. Catal.* 1988; **48**, 249-64.
[13] Z Xi, W Liu, G Cao, W Du, J Huang, K Cai and H Guo. Catalytic oxidation of naphthol by metalloporphyrins. *Cuihau Xuebao* 1986; **7**, 357-63.
[14] A Rezaeifard, I Sheikhshoaie, N Monadi and H Stoeckli-Evans. Synthesis, crystal structure, and catalytic properties of novel dioxidomolybdenum (VI) complexes with tridentate Schiff base ligands in the biomimetic and highly selective oxygenation of alkenes and sulfides. *Eur. J. Inorg. Chem.* 2010; **5**, 799-806.

[15] YD Zhao, DW Pang, Z Zong, JK Cheng, ZF Luo, CJ Feng, HY Shen and XC Zhung. Electochemical studies of antitumor drugs, fundamental electrochemical characteristics of an iron(III) complex and interaction with DNA. *Huaxe Xuebao* 1988; **56**, 178-83.
[16] RW Hay, PR Norman and F McLaren. Cobalt (II) and alkylcobalt(III) complexes of N,N′-bis(2-thioformyl-2-phenylvinyl)trimethylenediamine. A cobalt(II) oxygen carrier. *Inorg. Chim. Acta* 1980; **44**, 125-7.
[17] G Pascal, FA Lacroix, M Isabelle and N Keitaro. Synthesis, Crystal structures and molecular hyperpolarizabilities of a new Schiff base ligand, and its copper (II), nickel (II), and cobalt (II) metal complexes. *Inorg. Chim. Acta* 2004; **357**, 3825-35.
[18] I Sheikhshoaie and WMF Fabian. Theoretical insights into material properties of Schiff bases and related azo compounds. *Curr. Org. Chem.* 2009; **13**, 149-71.
[19] PN Prasad and DJ Williams. *Introduction to Non-Linear Optical Effects in Molecules and Polymers*. John Willy & Sons Inc., New York, 1991.
[20] YP Tian, CY Duan, CY Zhao and XZ You. Synthesis, Crystal structure and second-order optical nonlinearity of bis(2-chlorobenzaldehyde thiosemicarbazone) Cadmium halides (CdL_2X_2: X=Br, I). *Inorg. Chem*. 1997; **36**, 1247-52.
[21] W Kohn and LJ Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev*. 1958; **140**, A1133-8.
[22] AD Becke. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 1993; **98**, 5648-52.
[23] MJ Frisch, GW Trucks, HB Schlegel, GE Scuseria, MA Robb, JR Cheeseman, JA Montgomery Jr., T Vreven, KN Kudin, JC Burant, JM Millam, SS Iyengar, J Tomasi, V Barone, B Mennucci, M Cossi, G Scalmani, N Rega, GA Petersson, H Nakatsuji, M Hada, M Ehara, K Toyota, R Fukuda, J Hasegawa, M Ishida, T Nakajima, Y Honda, O Kitao, H Nakai, M Klene, X Li, JE Knox, HP Hratchian, JB Cross, C Adamo, J Jaramillo, R Gomperts, RE Stratmann, O Yazyev, AJ Austin, R Cammi, C Pomelli, JW Ochterski, PY Ayala, K Morokuma, GA Voth, P Salvador, JJ Dannenberg, VG Zakrzewski, S Dapprich, AD Daniels, MC Strain, O Farkas, DK Malick, AD Rabuck, K Raghavachari, JB Foresman, JV Ortiz, Q Cui, AG Baboul, S Clifford, J Cioslowski, BB Stefanov, G Liu, A Liashenko, P Piskorz, I Komaromi, RL Martin, DJ Fox, T Keith, MA Al-Laham, CY Peng, A Nanayakkara, M Challacombe, PMW Gill, B Johnson, W Chen, MW Wong and C Gonza. *Information Technology Services.* University of Wollongong, Gaussian Inc., Wallingford, CT.
[24] I Sheikhshoaie, SY Ebrahimipour and M Sheikhshoaee. Structural investigation of methanol {6-[(2-oxidopropyl)iminomethyl]phenolato}dioxidomolybdenum(VI) by X-ray crystallography and DFT calculations. *Walailak J. Sci. & Tech.* 2012, **9**, 207-16.