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Synthesis , Characterization and Computational Study of some New Schiff Base Derivative from 5,6-dinitro-1H-indene-1,3(2H)-dione

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ABSTRACT

Multifunctional Schiff base ligands from 5,6-dinitro-1H-indene-1,3(2H)-dione with aniline derivatives (Scheme 1) were synthesized. These Schiff base compounds have been characterized by C, H, N elemental analysis, FT-IR, and ¹H NMR spectroscopy. The structural and electronic properties of para-substituted phenyl have been investigated theoretically by performing semi-empirical molecular orbital theory at the level of PM3 of theory. The optimized structures, relative binding energies, atomic charges, position of HOMO and LUMO of the molecules are obtained.

Key word : Schiff base, 5,6-dinitro-1H-indene-1,3(2H)-dione

INTRODUCTION

A big challenge facing academia and industry is the relationship of modern societies to the environment that requires reinventing the manufacture and use of materials. Synthetic methodologies now a day should be designed to use and generate substances that possess little or no toxicity to human health and the environment. Schiff bases belong to a widely used group of organic intermediates important for production of specialty chemicals, e.g. pharmaceuticals, or rubber additives [1] and as amino protective groups in organic synthesis [2,3]. They also have uses as liquid crystals [4], and in analytical [5-7] medicinal [8] and polymer chemistry [9].

Conventionally Schiff bases have been prepared by refluxing mixtures of the amine and the carbonyl compound in an organic solvent, for example, ethanol or methanol [10], but variations are known, such as treatment of the same mixture at room temperature, refluxing the mixture in heptane in the presence of acetic acid [11], or azeotroping the mixture with benzene in a Dean-Stark apparatus in the presence of acid [12]. In general, ketones react more slowly than aldehydes and higher temperatures and longer reaction times are often required as a result. In addition, the equilibrium must often be shifted, usually by removal of the water, either azeotropically by distillation or with suitable drying agents [13]. In recent years, environmentally benign synthetic methods have received considerable attention and some solvent-free protocols have been developed [14]. Grinding together solid anilines and solid benzaldehydes yielded various kinds of benzylideneanilines [15]. The synthesis of primary imines by condensation of 2-hydroxylaryl ketones with ammonium iodide and piperidine under solvent free conditions [16].

In this work we have synthesized and characterized of some new Schiff base compounds Derived 5,6-dinitro-1H-indene-1,3(2H)-dione. The synthesis compounds have been studied theoretically by semi-empirical molecular orbital theory at the level of PM3 of theory.

MATERIALS AND METHODS**1. General:**

Melting points were uncorrected. NMR spectra were acquired with a Bruker Ultra Shield (^1H : 300 MHz) (University of AL-al-Bayt, Jordan). The chemical shifts were referenced to tetra methyl silane (TMS) as an internal standard. The elemental analysis were performed by using Euro Vector EA3000A (University of AL-al-Bayt, Jordan).

1.1 Synthesis of diimines:**General procedure:**

(0.01 mole) of 5,6-dinitro-1H-indene-1,3(2H)-dione (1) was dissolved in absolute ethanol in the presence of p-toluene sulphonic acid. Then, (0.02 mole) of aniline and its derivatives (2-6) were added and heated under reflux for (3) hrs. Then, the mixture was cooled in an ice bath for 2 hrs and yielded different coloured crystals. The residue was purified by recrystallization from benzene.

N,N'-(5,6-dinitro-1H-indene-1,3(2H)-diylidene)dianiline (2)

From aniline 70 % yield ; m.p. (170-172) $^{\circ}\text{C}$; CHN analysis for $\text{C}_{21}\text{H}_{14}\text{N}_4\text{O}_4$; C 65.28; H 3.65; N 14.50 Found; C 65.22; H 3.61; N 14.45. FT-IR spectra $\nu(\text{cm}^{-1})$ 1656 cm^{-1} (C=N). $\delta_{\text{H}}(\text{CDCl}_3)$ (8.272) ppm(2H,s,a); (7.080-7.384) ppm (10H,m,b,c,d); 1.575 ppm (2H,s,e).

N,N'-(5,6-dinitro-1H-indene-1,3(2H)-diylidene)bis(4-methylaniline) (3)

From 4-methyl aniline 79 % yield ; m.p. (100-102) $^{\circ}\text{C}$; CHN analysis for $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_4$; C 66.66; H 4.38; N 13.52 Found; C 66.59; H 4.36; N 13.50. FT-IR spectra $\nu(\text{cm}^{-1})$ 1674 cm^{-1} (C=N). $\delta_{\text{H}}(\text{CDCl}_3)$ (8.264)ppm(2H,s,a); (7.418-7.481) ppm (8H,m,b,c); 7.282 (s, CDCl_3); 3.751 ppm (6H,s,d); 2.175 ppm (2H,s,e) .

N,N'-(5,6-dinitro-1H-indene-1,3(2H)-diylidene)bis(4-methoxyaniline) (4)

From 4-methoxy aniline 90 % yield ; m.p. (88-90) $^{\circ}\text{C}$; CHN analysis for $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_6$; C 61.88; H 4.06; N 12.55 Found; C 61.80; H 4.58; N 12.51. FT-IR spectra $\nu(\text{cm}^{-1})$ 1654 cm^{-1} (C=N). $\delta_{\text{H}}(\text{CDCl}_3)$ (8.264) ppm(2H,s,a); (7.418-7.481) ppm (8H,m,b,c); 7.282 (s, CDCl_3); 3.751 ppm (6H,s,d); 2.175 ppm (2H,s,e).

N,N'-(5,6-dinitro-1H-indene-1,3(2H)-diylidene)bis(4-bromoaniline) (5)

From 4-bromo aniline 68 % yield ; m.p. (202-204) $^{\circ}\text{C}$; CHN analysis for $\text{C}_{21}\text{H}_{12}\text{N}_4\text{O}_4\text{Br}_2$; C 46.35; H 2.22; N 10.30 Found; C 46.28; H 2.20; N 10.29. FT-IR spectra $\nu(\text{cm}^{-1})$ 1637 cm^{-1} (C=N). $\delta_{\text{H}}(\text{CDCl}_3)$ (8.179) ppm(2H,s,a); (7.800-7.917) ppm (8H,m,b,c); 7.282 (s, CDCl_3); 2.175 ppm (2H,s,e).

N,N'-(5,6-dinitro-1H-indene-1,3(2H)-diylidene)bis(4-nitroaniline) (6)

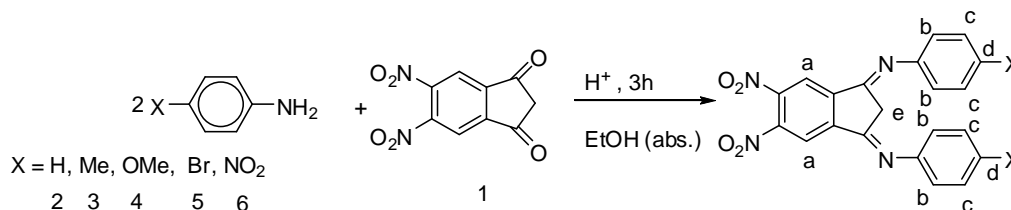
From 4-nitro aniline 65 % yield ; m.p. (250-252) $^{\circ}\text{C}$; CHN analysis for $\text{C}_{21}\text{H}_{12}\text{N}_6\text{O}_8$; C 52.95; H 2.54; N 17.64 Found; C 52.91; H 2.50; N 17.63. FT-IR spectra $\nu(\text{cm}^{-1})$ 1670 cm^{-1} (C=N). $\delta_{\text{H}}(\text{CDCl}_3)$ (7.800-7.917) ppm(6H,m,a,c); 7.282 (s, CDCl_3); (6.629-6.669) ppm (4H,d,b); 2.175 ppm (2H,s,e).

2. Computational methods

All theoretical calculations in this work were performed using the computational methods. Geometry optimization of the studied compounds was done by performing the semi-empirical molecular orbital theory at the level PM3 [17].

RESULTS AND DISCUSSION

Treatment of 5,6-di-nitro-1H-indene-1,3(2H)-dione (1) with aniline and its derivatives (4-6) in the presence of p-toluene sulphonic acid as catalyst in boiling ethanol gave, after purification by recrystallization from benzene, pure dimer imino derivatives in (65-90) % yield, as crystalline compounds, as shown in scheme 1, while the compounds (2) and (3) are prepared by Yoko et al. [18]. The structures of these products were established from their elemental analysis, FT-IR, C.H.N and ^1H NMR spectra. All the IR spectra of dimeric imine showed a peak at (1630-1637) cm^{-1} which appeared due to (C=N) stretching. All the ^1H NMR spectra of dimeric imine were characterized [19-21] by the presence of OCH_3 protons appeared at $\delta = 3.751$ ppm. The aliphatic protons (CH_2) to indane ring appeared at $\delta = 2.175$ ppm. The aromatic protons rings showed singlet or multiplet signal in the region $\delta = (7.800-8.272)$ ppm due to protons at a position. The other protons at b position for this rings showed doublet or multiplet signal within the range (6.629-7.917) ppm. The proton in c position showed multiplet signal in the region (7.080-7.917) ppm. The protons at d position for this rings showed multiplet signal within the range (7.080-7.384) ppm.



Scheme 1

Computational Study

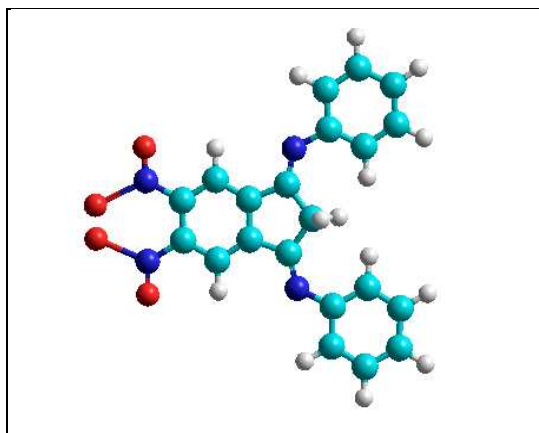
The optimized structures of the studied molecules are shown in Fig 1. The PM3 geometry optimizations yield planar structures for the synthesis compounds. The general geometries of molecule all compounds are very similar.

The total energy, highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO, respectively) energies and the energy band gap (LUMO–HOMO energy difference, ΔE) and the dipole moment, μ (in Debyes) for the studied molecules are given in Table 1.. The calculated dipole moment indicates that the studied molecules are pole. This means that these molecules may interact with its environmental, especially other polar molecules.

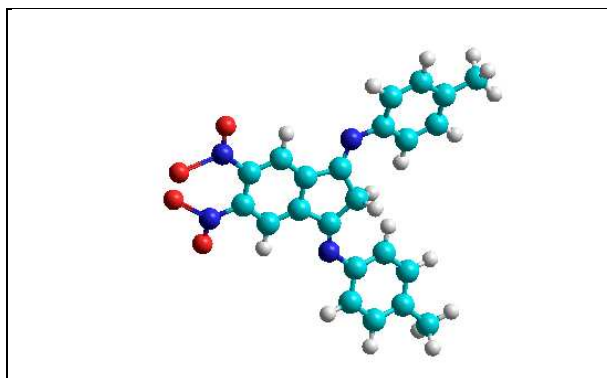
The spatial distributions of HOMO LUMO are shown in Fig. 2. In general the all molecules gave similar HOMO and LUMO orbitals.

Table1. The Total energy, MO energy of the lowest, highest, HOMO, LUMO, levels, ΔE (in au) and the dipole moment, μ (in Debyes) for the studied molecules

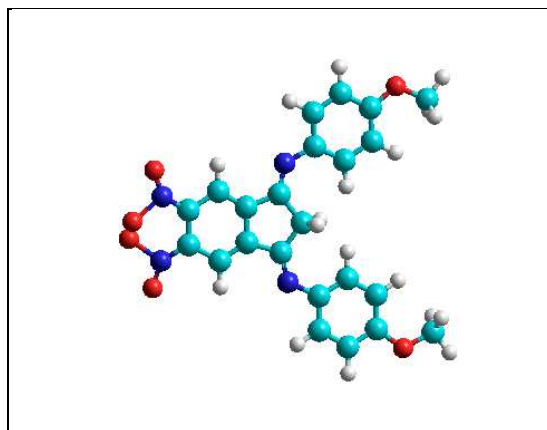
Mol.	Method	Total energy	HOMO	LUMO	ΔE	μ
2	PM3	-165.9633	-9.3259	-1.9048	-7.4211	8.085
3	PM3	-176.9682	-9.1654	-1.8626	-7.3028	8.639
4	PM3	-198.4870	-8.4927	-1.8264	-7.6663	7.846
5	PM3	-190.7813	-8.7277	-2.0080	-6.7197	3.647
6	PM3	-219.6923	-9.0959	-2.3972	-6.6987	4.895



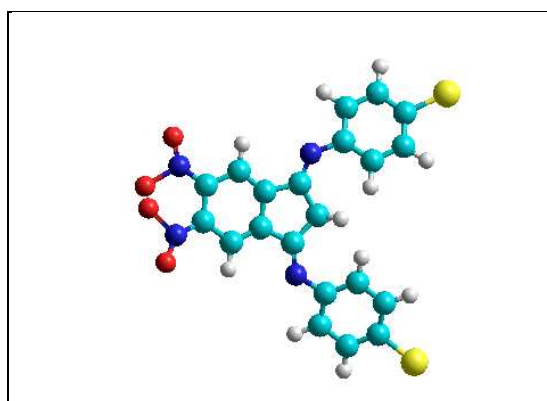
Geometry optimization (2)



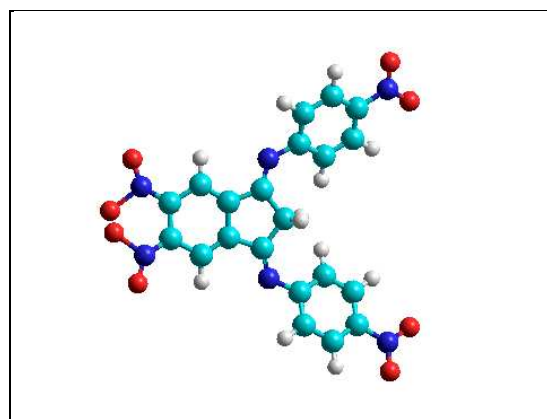
Geometry optimization (3)



Geometry optimization (4)

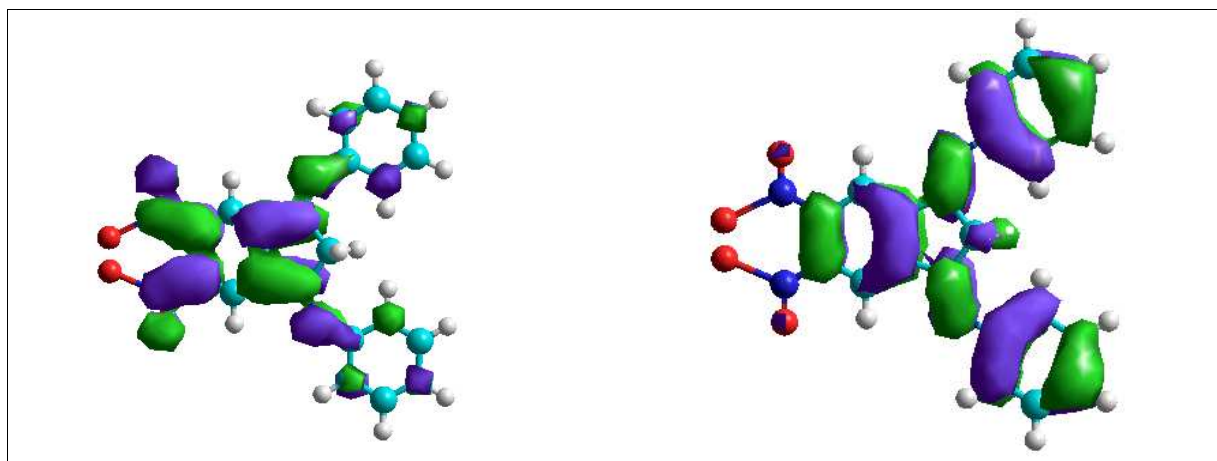


Geometry optimization (5)



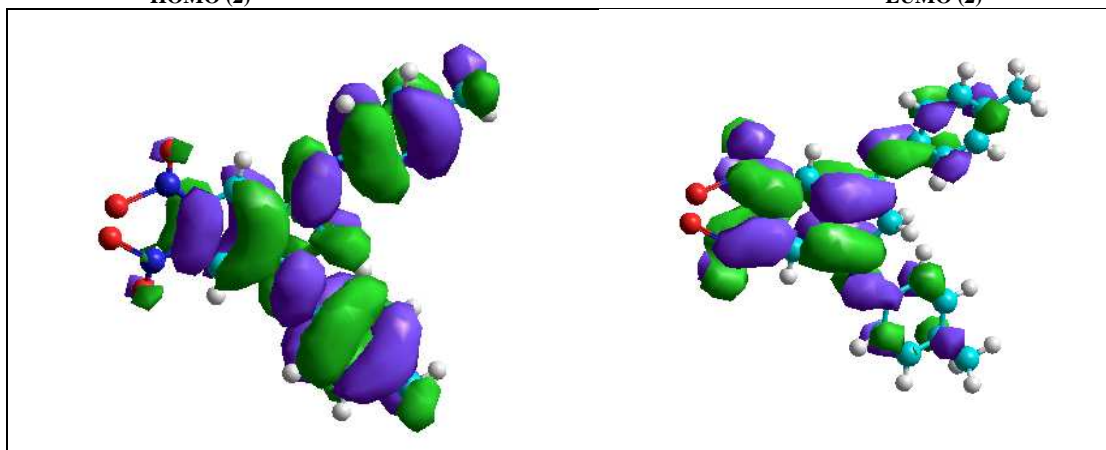
Geometry optimization (6)

Fig1. The optimized structure of the studied molecules optimization has been performed by PM3 method.



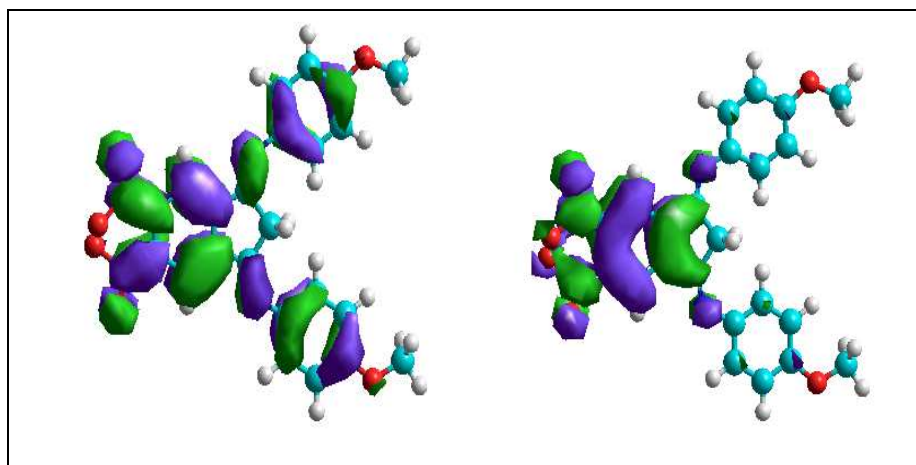
HOMO (2)

LUMO (2)



HOMO (3)

LUMO (3)



HOMO (4)

LUMO (4)

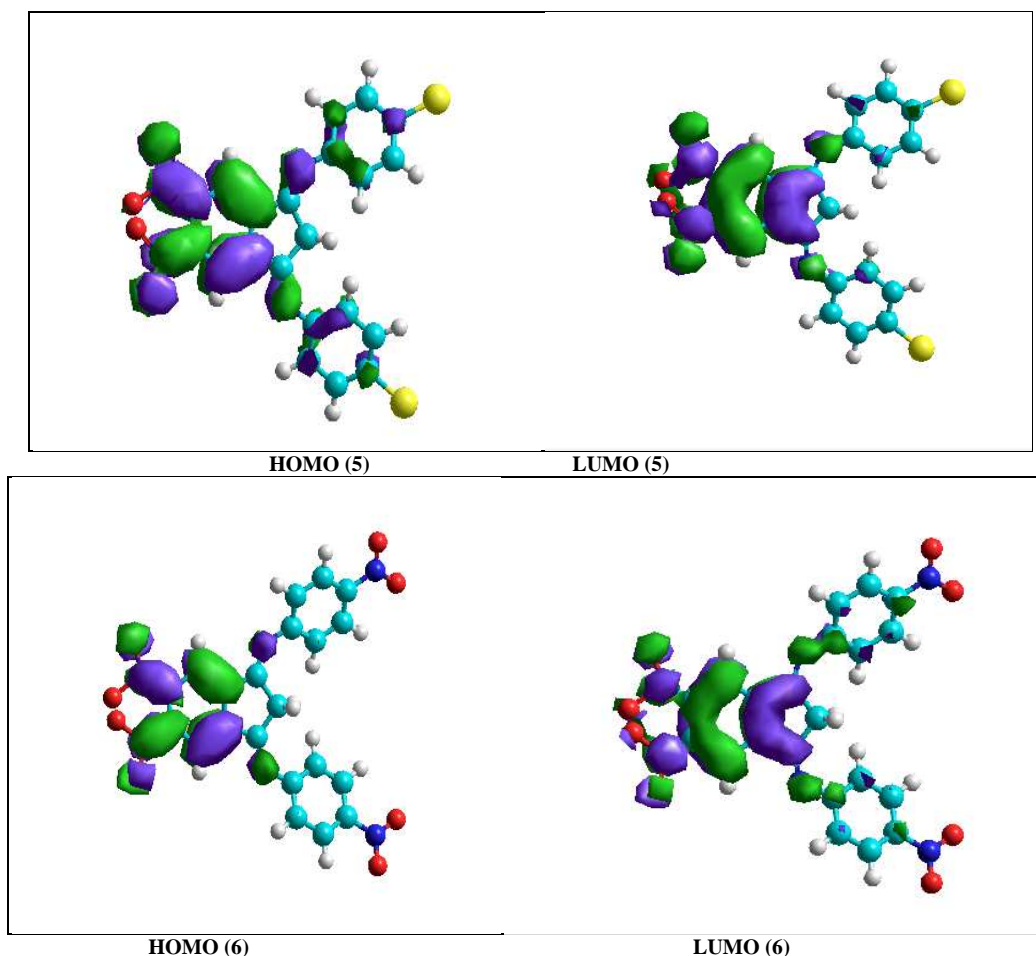


Fig 2. 3D HOMO and LUMO plots of the studied molecules

CONCLUSION

In conclusion, a rapid, high yield, simple, practical, economic, readily available system, and convenient procedure for the synthesis of Schiff base derived from 1,3-indandione and computational study, has been developed.

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