Synthesis, characterization and theoretical study for different substituted (1*E*,3*E*)-1,3-dibenzylidene urea

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ABSTRACT

Sequential substituted Schiff bases were prepared by direct condensation of urea and benzaldehyde or its substituents (o, m and p-bromo and hydroxy) as (1 : 2) mole ratio (urea : benzaldehyde or its substituents) , The prepared compounds characterized by infrared spectroscopy FT-IR and Thin layer chromatography T.L.C , the theoretical study for electronic structures for prepared compounds evaluated to study the effects of substituent and its position on the electronic structure. Our results indicate that the energy differences between the lowest unoccupied molecular orbital LUMO and the highest occupied molecular orbital HOMO are predominantly affected by the azomethene groups and its position in (1E,3E)-1,3-dibenzylidene urea conjugated system comparison with urea .

Keywords: AM1, HF, dibenzylidene urea, Bond order, HOMO, LUMO
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INTRODUCTION

Schiff base (CH=N) is a well-known linking groups used in connecting two core groups. Though, it provides a stepped core structure, yet it maintains molecular linearity, hence providing higher stability[1] . The molecular orbital (MO) is an important concept in chemistry, and molecular orbital theory is employed extensively to describe chemical behavior. Not only has MO theory become a ubiquitous set of tools used to explain chemical behavior, such as reactivity and kinetics, but it also provides an indispensable conceptual construct for the description of other phenomenon involving molecular electronic structure including charge transfer processes ,[2-5] photoexcitation, magnetism, and molecular electronics. In fact, it is quite common to extract trends in molecular behavior based on simple MO properties. For example, molecules with large HOMO-LUMO gaps are generally stable and unreactive; while those with small gaps are generally reactive[6-8]. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the two most important molecular orbitals. the energy of the HOMO is a good approximation to the negative experimental ionization potential (-IP).similarly, it suggests that the electron affinity(EA) for an N-electron system is equal to the negative of the LUMO energy [9] . In this paper we have prepared Sequential substituted Schiff bases compound of Urea(Fig.1) in order to establish the substituents effect and its position.
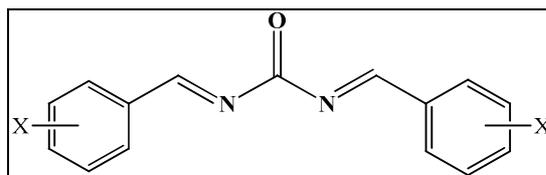

Figure 1.General Structure for prepared compounds

Comp.	A₁	A₂	A₃	A₄	A₅	A₆	A₇
X	H	*O*-OH	*m*-OH	*p*-OH	*O*-Br	*m*-Br	*p*-Br

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EXPERIMENTAL SECTION

Infrared spectra were recorded as KBr pellets on FT-IR 100 Fisher company thermo Scientific spectrometer , Melting points were recorded with Gallenkamp Melting point Apparatus and TLC solvent (Benzene : Ethanol : Diethylether) , (7 : 1 : 2) and development by using iodine crystals .

Synthesis of (1*E*,3*E*)-1,3-dibenzylidene urea
In 100 ml round bottom flask containing 25 ml absolute ethanol was stirred(16 mmol) of appropriate aldehyde with 5 drops Glacial acetic acid for 15 min. then 20 ml of ethanolic urea (8 mmol) was added , the mixture refluxed for 4 hr. the solvent was evaporate and precipitate was recrystallised with ethanol .

RESULTS AND DISCUSSION

1,3-dibenzylidene urea and its derivative identified by FT-IR spectrophotometer. The spectrums shows disappearance of stretching vibration (symmetry and asymmetry) for amino groups and appear of stretching vibrations for C=N at range (1581- 1624cm^{-1})[10] The results are given in table 1.

Table 1. FT-IR absorption bands for prepared Schiff bases Compounds (cm^{-1})

Comp.	υ O-H	υ C-H $_{Aro.}$	υ C=O	υ C=N	υ C-Br	υ C-O
urea	-	-	1669	-	-	-
A$_1$	-	3071	1678	1624	-	-
A$_2$	3442	3040	1687	1608	-	1182
A$_3$	3445	3025	1670	1581	-	1172
A$_4$	3431	3020	1668	1598	-	1240
A$_5$	-	3071	1653	1610	599	-
A$_6$	-	3060	1659	1610	610	-
A$_7$	-	3061	1660	1600	590	-

The purity of prepared compounds tested by Thin layer chromatography T.L.C with   using solvents (Benzene : Ethanol : Diethylether) (7 : 1 : 2) and development by iodine crystals . The results of retention factors R$_f$ are given in table 2.

Table 2. R$_f$ for prepared Schiff base Compounds

Comp.	A$_1$	A$_2$	A$_3$	A$_4$	A$_5$	A$_6$	A$_7$
R$_f$	0.60	0.65	0.60	0.50	0.59	0.59	0.53

The results for some physical properties such as Melting points , colors , IUPAC name and compounds symbols are given in table 3.

Table 3. physical properties for prepared Compounds

Comp.	IUPAC name	Formula	M.Wt.	M.p. ºC	Color
A$_1$	(1*E*,3*E*)-1,3-dibenzylidene urea	C$_{15}$H$_{12}$N$_2$O	236.09	77-79	White
A$_2$	(1*E*,3*E*)-1,3-bis(2-hydroxybenzylidene)urea	C$_{15}$H$_{12}$N$_2$O$_3$	268.27	120-123	Deep orange
A$_3$	(1*E*,3*E*)-1,3-bis(3-hydroxybenzylidene)urea	C$_{15}$H$_{12}$N$_2$O$_3$	268.27	80-83	Deep orange
A$_4$	(1*E*,3*E*)-1,3-bis(4-hydroxybenzylidene)urea	C$_{15}$H$_{12}$N$_2$O$_3$	268.27	60-63	Deep orange
A$_5$	(1*E*,3*E*)-1,3-bis(2-bromobenzylidene)urea	C$_{15}$H$_{10}$Br$_2$N$_2$O	394.06	204-206	White
A$_6$	(1*E*,3*E*)-1,3-bis(3-bromobenzylidene)urea	C$_{15}$H$_{10}$Br$_2$N$_2$O	394.06	185-188	White
A$_7$	(1*E*,3*E*)-1,3-bis(4-bromobenzylidene)urea	C$_{15}$H$_{10}$Br$_2$N$_2$O	394.06	229-231	White

Table 4: Calculated HOMO , LUMO, HOMO – LUMO gaps energies and some Electronic properties for hydroxy substituents

Comp.	HOMO (a.u.)	LUMO (a.u.)	HOMO – LUMO (a.u.)	μ	ω	η	*I*	A
Urea	-0.3870	0.0725	-0.459	0.157	0.114	0.229	0.387	-0.0725
A$_1$	-0.3542	-0.0333	-0.320	0.193	0.080	0.160	0.354	0.0333
A$_2$	-0.3345	-0.0425	-0.292	0.188	0.073	0.146	0.334	0.0425
A$_3$	-0.3382	-0.0378	-0.300	0.187	0.075	0.150	0.338	0.0378
A$_4$	-0.3374	-0.0317	-0.305	0.184	0.076	0.152	0.337	0.0317
A$_5$	-0.3489	-0.0362	-0.312	0.192	0.078	0.156	0.348	0.0362
A$_6$	-0.3566	-0.0418	-0.314	0.199	0.078	0.157	0.356	0.0418
A$_7$	-0.3558	-0.0451	-0.310	0.200	0.078	0.155	0.355	0.0451

μ=Electronegativity , ω=Electrophilcity , η=Hardness , I=Ionization potential , AElectronaffinity

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COMPUTATIONAL STUDY
All calculations were performed with ChemBio 3D Ultra 11.0.1. The ground-state geometries were fully optimized at AM1 theory (Austin Model1 is semiempirical method that is most often used to model organic molecules)using a 6-311G bases set .

The values HOMO,LUMO , HOMO-LUMO gaps and some Electronic properties of studied compounds are given in table 4. The electronic distribution in both HOMO and LUMO are given in table 7.

The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and HOMO - LUMO energy gaps was calculated , the molecules with large HOMO-LUMO gaps are generally stable and unreactive; while those with small gaps are generally reactive and the higher the HOMO energies, the easier it is for HOMO to donate electrons; the lower the LUMO energies, the easier it is for LUMO to accept electrons [6-8].Therefore all prepared compounds (A_2 , A_3 , A_4 , A_5 , A_6 , A_7) decreasing the HOMO-LUMO gaps comparing with $A_1$and urea compounds Table 5.

From the results data in table 4, it is obvious that the HOMO energies of A_1 are higher than other compounds studies and the energy gap of A_1 is smaller than other compounds studies. Consequently, the electrons transfer from HOMO to LUMO in A_1 is relatively easier than that in other compounds studies.

The Electron properties such as electron affinity *A* and Ionization potential *I* calculated by the following equations :
$A=(-E_{LUMO})$

$I=(-E_{HOMO})$

while absolute electronegativity **μ**, absolute hardness **η** and elctrophilcity **ω** calculated by the following equations:
$\mu=1/2(I+A)$

$\eta =1/2(I+A)$

$\omega= \mu^2/2 \eta$

The electron affinity and Ionization potential values increase with electron withdrawing groups (bromo substituents) particular on the *Para* position while decrease with electron donor groups (hydroxy substituents) particular on the *Para* position , the arrangement results are given in table 5.Hardness define the resistance of molecule to electronic distribution changes , therefore the hardness values indicate that the molecules with hydroxy substituents less hardness than the bromo substituents table 5. The molecule behaviors can be measured by the elctrophilcity **ω** , the high values of **ω** indicate that the molecule is electrophile while the law values of **ω** indicate that the molecule is nucleophile , the arrangement of elctrophilcity indicate that the molecules with hydroxy substituents less elctrophilcity and no effect of bromo position on the **ω** table 5. The electronegativity for prepared compounds have high values with bromo substituents and less with hydroxy substituents table 5.

Table 5. The arrangement results for calculate property

Property	Decreasing of property →
	Results of arrangement
HOMO – LUMO gap	Urea >A_1> A_6>A_5> A_7> A_4>A_3 > A_2
$A=(-E_{LUMO})$	A_7>A_2> A_6>A_3> A_5>A_1 > A_4> Urea
$I=(-E_{HOMO})$	Urea >A_6> A_7>A_1> A_5> A_3 >A_4 > A_2
$\eta =1/2(I+A)$	Urea >A_1> A_6 >A_5 > A_7> A_4 >A_3 > A_2
$\omega= \mu^2/2 \eta$	Urea >A_1> A_5= A_6= A_7> A_4 >A_3 > A_2
$\mu=1/2(I+A)$	A_7> A_6 >A_1 >A_5> A_2 >A_3 > A_4> Urea

Internuclear distances and bond order of molecule center performed at the Hartree-Fock (**HF**) level , Figure 2.General Structure for molecule center.
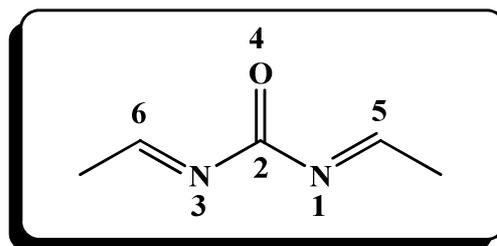
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Figure 2.General Structure for molecule center

The results for Internuclear distances and bond order are given in tables 6.

**Table 6. Bond Order and internuclear distances (Angs.)**

Comp.	Bond Order			internuclear distances (Angs.)		
	(CO)-N	C=O	C=N	N_1-C_2 , N_3-C_2	C_2-O_4	N_1-O_4 , N_3-O_4
Urea	0.903	1.752	-	1.3689	1.2080	2.2427
A_1	0.957	1.686	1.634	1.4260	1.2079	2.2998
A_2	0.936	1.700	1.517	1.4259	1.2079	2.2999
A_3	0.955	1.690	1.639	1.4260	1.2079	2.2998
A_4	1.006	1.719	1.297	1.4259	1.2080	2.3008
A_5	0.953	1.691	1.628	1.4259	1.2079	2.2996
A_6	0.954	1.692	1.650	1.4260	1.2079	2.2994
A_7	0.955	1.690	1.641	1.4260	1.2079	2.2995

CONCLUSION

The study indicate that all prepared substituted compounds decreasing the HOMO-LUMO gaps comparing with urea and hydroxy groups decreasing the HOMO-LUMO gaps more than bromo substituted regardless of position , the hydroxy substituted compounds hardness results indicate that this compounds more aromatic comparison with bromo substituted compounds .

Table 7. The electronic distribution in both HOMO and LUMO

Comp.	HOMO	LUMO
Urea		
A_1		
A_2		
A_3		

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A₄		
A₅		
A₆		
A₇		
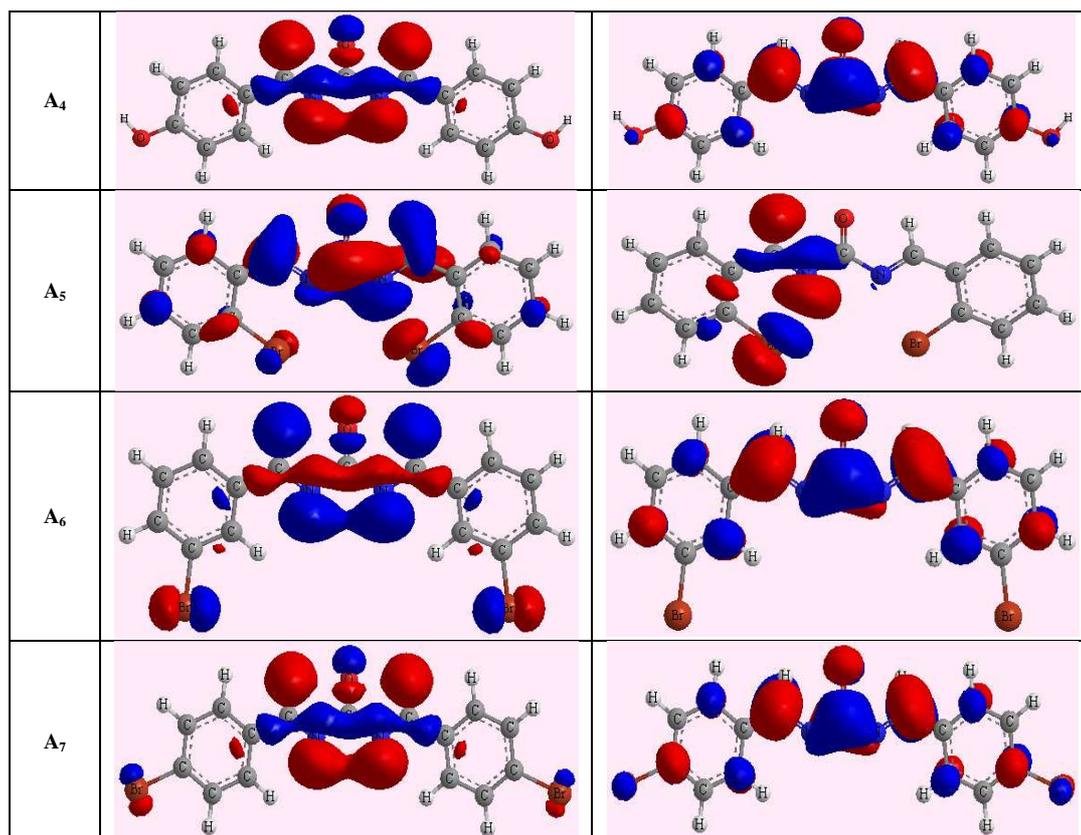
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