

Ab initio calculations and structure of three acyclic bis(acetyl acetone)imine derivatives

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Abstract:

The possible tautomers of $(acac)_2u$, $(acac)_2tu$, and $(acac)_2u.meth$ molecules are studied theoretically at ab initio method using minimal (STO-3G) level of theory. It is found that the keto-imino tautomer is the dominated one among these possible tautomers. Total dipole moments, highest occupied and lowest unoccupied molecular orbitals energies (E_{HOMO} and E_{LUMO} respectively), and frontier molecular orbital energy gap ($E_{LUMO}-E_{HOMO}$) are calculated for all the tautomers, and reliable comparisons among them have been carried to conclude chemical reactivities, polarities, and then the stabilities. Four synthetic routes yielding $(acac)_2u.meth$ have been presented with calculation Gibbs free energies of formation to know tendencies of these reactions to occur. Also structural parameters of ab initio-calculated optimized structures of keto-imino tautomer for both $(acac)_2u$ and $(acac)_2tu$ molecules are calculated.

حسابات Ab initio وتركيب ثلاث مشتقات من ثنائي (أسيتايل أسيتون) إيمين غير الحلقية

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المخلص:

درست نظريا التوتوماتر المحتملة لـ $(acac)_2u$ ، و $(acac)_2tu$ ، و $(acac)_2u.meth$ باستخدام طريقة ab initio وعند المستوى minimal (STO-3G) من النظرية. وجد أن شكل الكيتو-إيمينو هو الشكل السائد من بين التوتوماتر المحتملة. حسبت لكل التوتوماتر عزوم ثنائي

القطب الكلية، وطاقتي أعلى اوربيتال جزئي مشغول واطماً اوربيتال جزئي غيرمشغول (E_{HOMO} و E_{LUMO} على التوالي)، و فجوة الطاقة الاوربيتالية الجزئية الحدودية ($E_{\text{HOMO}}-E_{\text{LUMO}}$)، وقد أجريت المقارنات بينها لإستنتاج الفعالية الكيميائية، والقطبية، ومن ثم استقرارياتها. لقد اوجدت أربعة مسالك تخليقية لـ $(\text{acac})_2\text{u.meth}$ مع حساب طاقات جيبس الحرة للتكوين لمعرفة ميول تلك التفاعلات في الحدوث. كذلك حسبت بطريقة *ab initio* الخصائص التركيبية لتركيب الكيتو-إيمينو للجزيئين $(\text{acac})_2\text{u}$ ، و $(\text{acac})_2\text{tu}$.

1. Introduction:

A number of studies has been made on bis (acetyl acetone) ethylenediimines and related compounds to determine the structural features of the ligands and their metal complexes [1-6].

The ligands bis (acetyl acetone) ethylmethylethylenediimine ($\text{H}_2\text{AA}_2\text{EMen}$), bis (trifluoroacetylacetone) ethylmethylethylenediimine ($\text{H}_2\text{F}_3\text{AA}_2\text{EMen}$), and bis (trifluoroacetylmesityloxi) ethylmethylethylenediimine ($\text{H}_2\text{F}_3\text{AM}_2\text{EMen}$) have been prepared and characterized using IR, $^1\text{H-NMR}$, and mass spectroscopic techniques. The IR of these reagents shows one to two weak bands within $3300-3100\text{ cm}^{-1}$ and a broad and strong band within $1630-1580\text{ cm}^{-1}$ due to hydrogen bonded NH and C=O groups respectively[7].

Also the $^1\text{H-NMR}$ of the molecules ($\text{H}_2\text{AA}_2\text{EMen}$) and ($\text{H}_2\text{F}_3\text{AA}_2\text{EMen}$) show a doublets, but ($\text{H}_2\text{F}_3\text{AM}_2\text{EMen}$) molecule has a triplet within δ 11.0-11.3 ppm due to the NH protons which (besides the IR evidences) indicate to the domination of the keto-amine tautomers of these molecules [7].

The IR spectrum of bis (acetyl acetone) o-dianisidine shows a medium intensity band [8] at 1600 cm^{-1} which is the carbonyl stretching frequency in the keto form of the mentioned ligand. The 1560 cm^{-1} is due to C=C & C=N stretching and a very strong band at 1220 cm^{-1} is due to the hydroxyl group in hydrogen bonding in enol form at the ligand[9].

$^1\text{H-NMR}$, IR, Mass techniques and x-ray besides theoretical density functional theory (DFT)-B3LYP/6-31G* calculations are used to analyze the molecule 4-[(2-[(1E)-1-methyl-3-oxobutylidene]amino)ethyl]imino] pentan-2-one which proved that the keto-amine tautomer is the

dominated form[10]. Similar conclusion has been drawn for one analogue compound; the 3,10-di-[2-(2-pyridyl)-ethyl]-bis-(acetyl-acetone)ethylenediimine[11].

In this work, the calculated geometry using the Ab initio method considers only the gas phase, where the molecule is free of interactions [14]. Total dipole moments, highest occupied and lowest unoccupied molecular orbitals energies (E_{HOMO} and E_{LUMO} respectively), and frontier molecular orbital energy gap ($E_{\text{LUMO}}-E_{\text{HOMO}}$) are calculated for all the tautomers of $(\text{acac})_2\text{u}$, $(\text{acac})_2\text{tu}$, and $(\text{acac})_2\text{u.meth}$ molecules. Also Bonds lengths and angles of bonds of Ab initio-calculated optimized structures of keto-imino tautomer for both $(\text{acac})_2\text{u}$ and $(\text{acac})_2\text{tu}$ molecules are calculated.

2. Computational Method:

All calculations were carried out using the HyperChem 8.02 suite of Quantum chemistry/Molecular Mechanics programs with standard parameters [12] running on windows xp platform 2GHz Intel Pentium IV CPU-personal computer.

To save computational time, initial optimization was carried out with the molecular mechanics (MM) methods using the AMBER force fields. The lowest energy conformations of the molecules obtained by MM method were further optimized by Ab initio (at minimal (STO-3G) level) calculations [13] employing the Polak Ribiere optimizer.

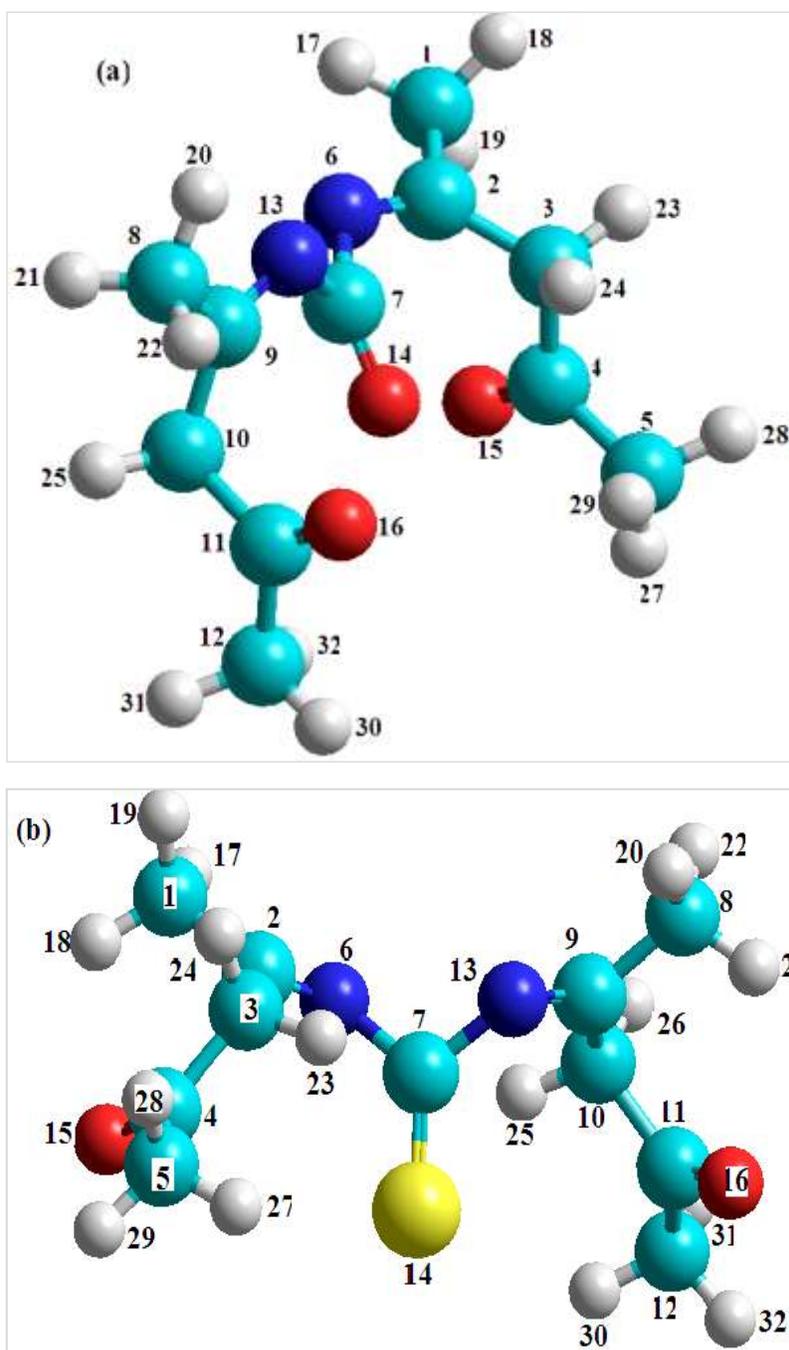
Results and Discussion:

The possible tautomers of $(\text{acac})_2\text{u}$, $(\text{acac})_2\text{tu}$, and $(\text{acac})_2\text{u.meth}$ molecules are studied theoretically at ab initio method using minimal (STO-3G) level of theory. From table 1 it could be seen that the

keto-imino tautomer for each of the three studied compounds has the less energy and accordingly has more stability (and so dominated tautomer) in comparison with other tautomers [15], although there are little differences in energy among tautomers for each molecule. Figure 1 shows the calculated structures of the most dominated proposed tautomers.

Table 1. Calculated total energies (10^{-3} kCal/mol) of tautomers of studied molecules.

Tautomers	(acac) ₂ u	(acac) ₂ tu	(acac) ₂ u.meth
Keto-imino	-470.459	-670.828	-482.407
Imino-enol	-470.424	-670.796	-482.375
Keto-amine	-470.449	-670.821	-482.388



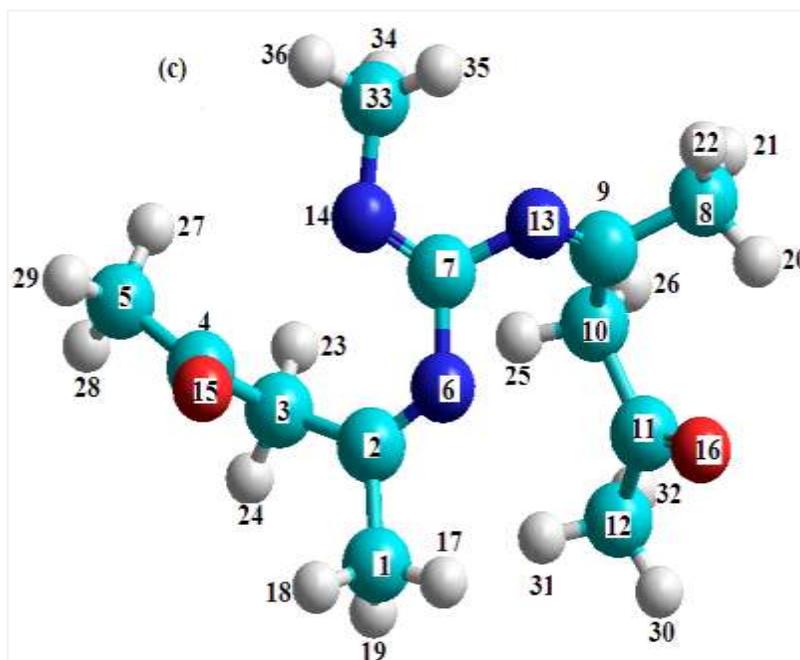


Figure 1. Ab initio-calculated optimized structures of the dominated tautomers for:(a):(acac)₂u,(b):(acac)₂tu, and (c):(acac)₂u.meth molecules using minimal (STO-3G) level of theory. Element colors in above molecules are: cyan for carbon, white for hydrogen, blue for nitrogen, red for oxygen, and yellow for sulfur, where (acac)₂u: H₃C.C(=O)CH₂.C(CH₃)=N.C(=O)N=C(CH₃)CH₂.C(=O)CH₃;(acac)₂tu: H₃C.C(=O)CH₂.C(CH₃)=N.C(=S)N=C(CH₃)CH₂.C(=O)CH₃;and(acac)₂u.meth:H₃C.C(=O)CH₂.C(CH₃)=N.C(=N.CH₃)N=C(CH₃)CH₂.C(=O)CH₃ .

The total dipole moments, highest occupied and lowest unoccupied molecular orbitals energies (E_{HOMO} and E_{LUMO} respectively), and frontier molecular orbital energy gap ($E_{\text{LUMO}}-E_{\text{HOMO}}$) are calculated for all the proposed tautomers and are presented in tables 2, 3, and 4. Among the possible tautomers of (acac)₂u, the dominated keto-imino tautomer is the lowest polarity while imino-enol tautomer is the higher polarity among them. The presence of sulfur or N-CH₃ instead of oxygen in binding moiety between the two acetyl acetone in (acac)₂tu, and (acac)₂u.meth molecules led to make imino-enol and keto-imino tautomers respectively are the highest polarities in comparison with both the rest tautomers of each the two molecules and keto-imino tautomer of (acac)₂u .

The Eigen values of LUMO and HOMO and their energy gap reflect the chemical reactivity of the molecule. Because LUMO is as an electron

acceptor, so its energy represents the ability to accept an electron, while HOMO energy (HOMO is an electron donor) represents the ability to donate an electron, so the smaller $E_{\text{LUMO}}-E_{\text{HOMO}}$ means the easier for HOMO electrons to be excited, and the higher HOMO energies mean the easier for HOMO to donate electrons. In contrast, the lower LUMO energies make easier to LUMO to accept electrons [16].

The highest value of $E_{\text{LUMO}}-E_{\text{HOMO}}$ (14.117 kCal/mol) was for keto-imino tautomer of (acac)₂u accompanied by the lowest value of total dipole moment (0.908 Debye), so it has the lowest chemical reactivity among the tautomers of all molecules. In contrast the imino-enol tautomer of (acac)₂tu has both the lowest value of $E_{\text{LUMO}}-E_{\text{HOMO}}$ (11.163 kCal/mol) and highest total dipole moment (7.107 Debye) which make it has

the highest chemical reactivity and low kinetic stability [17].

Table 2. Calculated, dipole moments (in Debye), energies of HOMO and LUMO levels (in eV), and $E_{\text{LUMO}}-E_{\text{HOMO}}$ of (acac)_{2u}.

Tautomers of (acac) _{2u}	Total Dipole moments	E_{HOMO}	E_{LUMO}	$E_{\text{LUMO}}-E_{\text{HOMO}}$
Keto-imino	0.908	-8.137	5.980	14.117
Imino-enol	3.233	-6.817	6.482	13.300
Keto-amine	1.397	-7.249	6.163	13.413

Table 3. Calculated, dipole moments (in Debye), energies of HOMO and LUMO levels (in eV), and $E_{\text{LUMO}}-E_{\text{HOMO}}$ of (acac)_{2tu}.

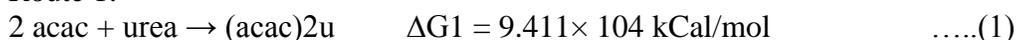
Tautomers of (acac) _{2tu}	Total Dipole moments	E_{HOMO}	E_{LUMO}	$E_{\text{LUMO}}-E_{\text{HOMO}}$
Keto-imino	2.861	-6.323	5.211	11.535
Imino-enol	7.107	-5.723	5.439	11.163
Keto-amine	1.362	-6.105	5.552	11.658

Table 4. Calculated, dipole moments (in Debye), energies of HOMO and LUMO levels (in eV), and $E_{\text{LUMO}}-E_{\text{HOMO}}$ of (acac)_{2u.meth}.

Tautomers of (acac) _{2u.meth}	Total Dipole moments	E_{HOMO}	E_{LUMO}	$E_{\text{LUMO}}-E_{\text{HOMO}}$
Keto-imino	5.419	-7.718	6.109	13.827
Imino-enol	3.901	-6.415	6.149	12.564
Keto-amine	1.063	-6.625	6.341	12.967

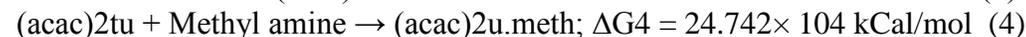
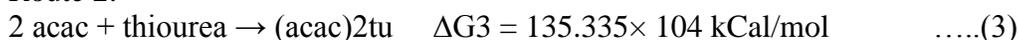
There are four synthetic routes to yield (acac)_{2u.meth} which are presented in equations below (1-8). Because they give useful indications of the tendencies of reactions to occur, Gibbs free energies of formation for mentioned reactions are calculated. Also they give us informations on the relative stability of compounds. All reactions (1-8) are with positive Gibbs free energies; therefore we may conclude that neither of these reactions will be spontaneous [18]. It can be seen from these reactions that routes 1 and 3 have the same Gibbs free energies and also is the case for routes 2 and 4, but because both later routes have smaller value of Gibbs free energy of formation than do routes 3 and 4, we may conclude that routes 1 and 3 are thermodynamically favorable [18].

Route 1:



$$\Delta G_{\text{Route 1}} = 14.116 \times 10^4 \text{ kCal/mol}$$

Route 2:



$$\Delta G_{\text{Route 2}} = 34.154 \times 10^4 \text{ kCal/mol}$$

Route 3:



$$\Delta G_{\text{Route 3}} = 14.116 \times 10^4 \text{ kCal/mol}$$

Route 4:



$$\Delta G_{\text{Route 4}} = 34.154 \times 10^4 \text{ kCal/mol}$$

It seems from above reactions, that both the formation of bis-schiff base (acac)₂u from reaction of two acetyl acetone molecules with urea and change of the oxygen atom of the binding unit in (acac)₂u into azomethine across the next reaction to yield finally (acac)₂u.meth are (rote 1) endothermic reactions, need the same energy, and are in the same thermodynamic preference with the opposite route 3 which clearly includes formation the Schiff base (u.meth) from reaction of Urea

with methyl amine and then the reaction of the resulting u.meth with two acetyl acetone molecules to bind them across formation two azomethine groups yielding the final ligand (acac)₂u.meth and the same case is valid for routes 2 and 4.

Bonds lengths and angles of bonds of ab initio-calculated optimized structures of keto-imino tautomer for both (acac)₂u and (acac)₂u molecules are calculated and presented in tables 5 and 6.

Table 5 : (a) and (b). Structural parameters of ab initio-calculated optimized structure of keto-imino tautomer for (acac)₂u molecule.

(a)

Bond	Value of bond length (°A)	Bond	Value of bond length (°A)
C(1)-C(2)	1.53008	C(7)-N(13)	1.46887
C(1)-H(17)	1.0844	N(13)=C(9)	1.28207
C(1)-H(18)	1.08738	C(9)-C(8)	1.52983
C(1)-H(19)	1.08751	C(8)-H(20)	1.08444
C(2)-C(3)	1.53785	C(8)-H(21)	1.08742
C(2)=N(6)	1.28181	C(8)-H(22)	1.08755
C(3)-C(4)	1.55461	C(9)-C(10)	1.53756
C(3)-H(23)	1.08867	C(10)-H(25)	1.08857
C(3)-H(24)	1.08693	C(10)-H(26)	1.08695
C(4)=O(15)	1.21734	C(10)-C(11)	1.55461
C(4)-C(5)	1.54024	C(11)=O(16)	1.21733
C(5)-H(27)	1.08508	C(11)-C(12)	1.5401
C(5)-H(28)	1.08635	C(12)-H(30)	1.08508
C(5)-H(29)	1.08654	C(12)-H(31)	1.08638
N(6)-C(7)	1.46899	C(12)-H(32)	1.08658
C(7)=O(14)	1.21994		

(b)

Bond Angle	Value of bond Angle (°)	Bond Angle	Value of bond Angle (°)
H(17)-C(1)-H(18)	109.233	O(14)=C(7)-N(13)	124.723
H(17)-C(1)-H(19)	109.28	O(14)=C(7)-N(13)=C(9)	-42.9564
H(18)-C(1)-H(19)	108.234	H(20)-C(8)-C(9)	110.058
H(17)-C(1)-C(2)	110.054	H(21)-C(8)-C(9)	110.232
H(18)-C(1)-C(2)	110.239	H(22)-C(8)-C(9)	109.762
H(19)-C(1)-C(2)	109.768	C(8)-C(9)=N(13)	117.765
C(1)-C(2)=N(6)	117.781	H(20)-C(8)-C(9)=N(13)	-0.77401
N(6)=C(2)-C(3)	126.606	H(21)-C(8)-C(9)=N(13)	119.784
N(13)=C(9)-C(10)	126.599	H(22)-C(8)-C(9)=N(13)	-121.095
N(6)-C(7)-N(13)	110.58	C(8)-C(9)=N(13)-C(7)	177.707
H(18)-C(1)-C(2)=N(6)	119.737	C(10)-C(9)=N(13)-C(7)	-1.71315
H(19)-C(1)-C(2)=N(6)	-121.127	C(9)=N(13)-C(7)	117.693
H(17)-C(1)-C(2)=N(6)	-0.815627	N(13)=C(9)-C(10)-C(11)	86.6155
C(1)-C(2)=N(6)-C(7)	177.699	C(8)-C(9)-C(10)	115.634
C(3)-C(2)=N(6)-C(7)	-1.72296	C(9)-C(10)-C(11)	111.619
C(2)-C(3)-C(4)	111.65	H(25)-C(10)-H(26)	107.643

Continued (b)

C(2)=N(6)-C(7)	117.689	C(10)-C(11)-C(12)	114.952
N(6)=C(2)-C(3)-C(4)	86.5697	C(10)-C(11)-O(16)	122.117
C(1)-C(2)-C(3)	115.61	C(12)-C(11)-O(16)	122.928
H(23)-C(3)-H(24)	107.643	C(9)-C(10)-C(11)-C(12)	-162.709
C(3)-C(4)-C(5)	114.953	H(30)-C(12)-C(11)=O(16)	3.35608
C(3)-C(4)=O(15)	122.113	H(31)-C(12)-C(11)=O(16)	123.917
C(5)-C(4)=O(15)	122.932	H(32)-C(12)-C(11)=O(16)	-116.779
C(2)-C(3)-C(4)-C(5)	-162.276	H(30)-C(12)-C(11)	110.051
H(27)-C(5)-C(4)=O(15)	3.48282	H(31)-C(12)-C(11)	110.239
H(28)-C(5)-C(4)=O(15)	124.05	H(32)-C(12)-C(11)	109.817
H(29)-C(5)-C(4)=O(15)	-116.647	H(30)-C(12)-H(31)	109.24
H(27)-C(5)-C(4)	110.051	H(30)-C(12)-H(32)	109.114
H(28)-C(5)-C(4)	110.235	H(32)-C(12)-H(31)	108.345
H(29)-C(5)-C(4)	109.805	C(9)=N(13)-C(7)=O(14)	-42.9564
H(27)-C(5)-H(29)	109.116	N(6)-C(7)=O(14)	124.697
H(27)-C(5)-H(28)	109.247	H(20)-C(8)-H(21)	109.239
H(28)-C(5)-H(29)	108.353	H(20)-C(8)-H(22)	109.289
C(2)=N(6)-C(7)=O(14)	-42.989	H(21)-C(8)-H(22)	108.228

Table 6 : (a) and (b). Structural parameters of ab initio-calculated optimized structure of keto-imino tautomer for (acac)₂ tu molecule.

(a)

Bond	Value of Bond length (°A)	Bond	Value of Bond length (°A)
C(1)-C(2)	1.53078	C(7)-N(13)	1.45772
C(1)-H(17)	1.08431	N(13)=C(9)	1.27752
C(1)-H(18)	1.08713	C(9)-C(8)	1.53086
C(1)-H(19)	1.08734	C(8)-H(20)	1.08426
C(2)-C(3)	1.53651	C(8)-H(21)	1.08701
C(2)=N(6)	1.2275	C(8)-H(22)	1.08725
C(3)-C(4)	1.55412	C(9)-C(10)	1.53656
C(3)-H(23)	1.08679	C(10)-H(25)	1.08676
C(3)-H(24)	1.08927	C(10)-H(26)	1.08925
C(4)=O(15)	1.21746	C(10)-C(11)	1.554
C(4)-C(5)	1.54091	C(11)=O(16)	1.21746
C(5)-H(27)	1.08637	C(11)-C(12)	1.54088
C(5)-H(28)	1.08627	C(12)-H(30)	1.08643
C(5)-H(29)	1.08498	C(12)-H(31)	1.08641
N(6)-C(7)	1.45729	C(12)-H(32)	1.08504
C(7)=O(14)	1.59197		

(b)

Bond Angle	Value of Bond Angle (°)	Bond Angle	Value of Bond Angle (°)
H(17)-C(1)-H(18)	109.227	O(14)= C(7)- N(13)	125.747
H(17)-C(1)-H(19)	109.152	O(14)= C(7)-N(13)=C(9)	76.9511
H(18)-C(1)-H(19)	108.285	H(20)-C(8)-C(9)	109.991
H(17)-C(1)-C(2)	109.997	H(21)-C(8)-C(9)	109.874
H(18)-C(1)-C(2)	109.889	H(22)-C(8)-C(9)	110.254
H(19)-C(1)-C(2)	110.257	C(8)-C(9)=N(13)	118.134
C(1)-C(2)=N(6)	118.146	H(20)-C(8)-C(9)=N(13)	-0.489425
N(6) = C(2)- C(3)	126.272	H(21)-C(8)-C(9)=N(13)	119.793
N(13) = C(9)- C(10)	126.277	H(22)-C(8)-C(9)=N(13)	-120.923
N(6)- C(7)- N(13)	108.493	C(8)-C(9)=N(13)-C(7)	-179.663

Continued (b)

H(18)-C(1)-C(2)=N(6)	119.801	C(10)-C(9)=N(13)-C(7)	0.142286
H(19)-C(1)-C(2)=N(6)	-120.914	C(9)=N(13)-C(7)	120.923
H(17)-C(1)-C(2)=N(6)	-0.485159	N(13)=C(9)-C(10)-C(11)	-103.327
C(1)-C(2)=N(6)-C(7)	-179.625	C(8)-C(9)-C(10)	115.589
C(3)-C(2)=N(6)-C(7)	0.161402	H(25)-C(10)-H(26)	107.471
C(2)-C(3)-C(4)	112.124	C(9)-C(10)-C(11)	112.125
C(2)=N(6)-C(7)	120.931	C(10)-C(11)-C(12)	114.831
N(6)=C(2)-C(3)-C(4)	-103.051	C(10)-C(11)-O(16)	122.48
C(1)-C(2)-C(3)	115.582	C(12)-C(11)-O(16)	122.687
H(23)-C(3)-H(24)	107.465	C(9)-C(10)-C(11)-C(12)	170.04
C(3)-C(4)-C(5)	114.847	H(30)-C(12)-C(11)=O(16)	117.234
C(3)-C(4)=O(15)	122.462	H(31)-C(12)-C(11)=O(16)	-123.443
C(5)-C(4)=O(15)	122.689	H(32)-C(12)-C(11)=O(16)	-2.95281
C(2)-C(3)-C(4)-C(5)	169.967	H(30)-C(12)-C(11)	110.057
H(27)-C(5)-C(4)=O(15)	117.123	H(31)-C(12)-C(11)	110.222
H(28)-C(5)-C(4)=O(15)	-123.55	H(32)-C(12)-C(11)	110.009
H(29)-C(5)-C(4)=O(15)	-3.05963	H(30)-C(12)-H(31)	108.248
H(27)-C(5)-C(4)	109.055	H(30)-C(12)-H(32)	109.055
H(28)-C(5)-C(4)	110.219	H(32)-C(12)-H(31)	109.215
H(29)-C(5)-C(4)	110.004	C(9)=N(13)-C(7)=O(14)	76.9511
H(27)-C(5)-H(29)	109.055	N(6)-C(7)=O(14)	125.761
H(27)-C(5)-H(28)	108.253	H(20)-C(8)-H(21)	109.235
H(28)-C(5)-H(29)	109.219	H(20)-C(8)-H(22)	109.161
C(2)=N(6)-C(7)=O(14)	76.8138	H(21)-C(8)-H(22)	108.293

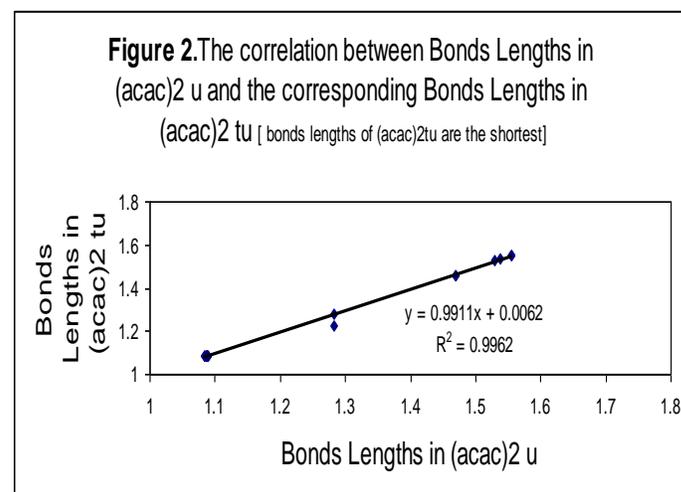
As shown in 5 and 6, it seems that C=S bond (1.59197 Å) in the binding unit of (acac)₂tu is longer than its corresponding C=O bond (1.21994 Å) of (acac)₂u, so it is a good leaving group and energetically more reactive in chemical reactions (especially substitution reactions).

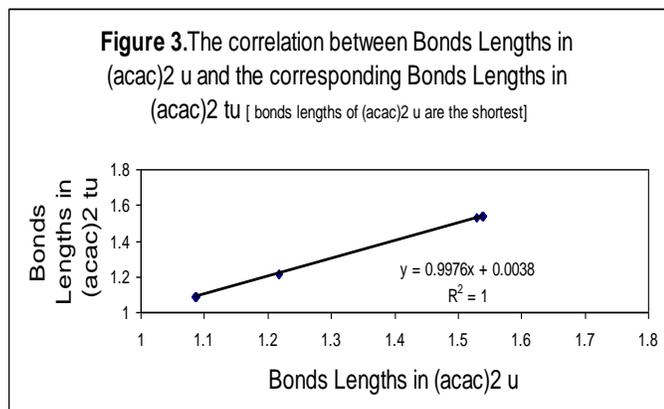
Both bonds C(4)=O(15) and C(11)=O(16) in (acac)₂tu have the same lengths and also they still longer a little than their corresponding bonds in (acac)₂u.

It can be seen that the most of bonds which are close to C=S group in (acac)₂tu are shorter than their corresponding bonds in (acac)₂u except both bonds C(1)-C(2) and C(9)-C(10). Thus the following bonds: C(7)-N(13), N(6)-C(7), C(2)=N(6), N(13)=C(9), C(9)-C(8), C(1)-H(17), C(1)-H(18), C(1)-H(19), C(1)-H(20), C(8)-H(21), C(8)-H(22), C(2)-C(3), C(3)-H(23), C(10)-H(25), C(3)-C(4), C(10)-C(11), C(5)-H(28), C(5)-H(29), and C(12)-H(32) in (acac)₂tu are shorter than their corresponding bonds in (acac)₂u, so they appear at longer wave numbers in infrared spectrum of (acac)₂tu[19].

In contrast, another relationship has found among bonds lengths of both (acac)₂u and (acac)₂tu molecules that the bonds which are far from C=S group are longer than their corresponding bonds in (acac)₂u.

These longer bonds are C(1)-C(2), C(9)-C(10), C(3)-C(24), C(10)-C(26), C(4)-C(15), C(11)-C(16), C(4)-C(5), C(11)-C(12), C(5)-C(27), C(12)-C(30), and C(12)-C(31). Both mentioned relationships are presented respectively in figures 2 and 3 below. The values of the correlation coefficients, 0.9911 and 1, provide very good linearity between bonds lengths in (acac)₂u and the corresponding bonds lengths in (acac)₂tu.





Because both bonds C(3)-H(23), and C(10)-H(25) in (acac)₂tu are shorter than the corresponding bonds in (acac)₂u, and bonds C(3)-H(24), and C(10)-H(26) are longer than the corresponding bonds in (acac)₂u, so the substitution reactions at the C(3) and C(10) atoms in both (acac)₂u and (acac)₂tu will be at the same strength[20].

Both (acac)₂u, and (acac)₂tu as diimines molecules are as Schiff bases which are subject to catalyzed and non-catalyzed hydrolysis, and because of both C(2)=N(6), and C(9)=N(13) in (acac)₂tu molecule are shorter, so (acac)₂tu suffers less hydrolysis than do (acac)₂u [17].

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