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An Initio Theoretical Study for the Electronic Spectra of β -Thioxoketones

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Abstract: Problem statement: β -thioxoketones exist as equilibrium mixtures of the tautomeric enol and enethiol forms which interconvert very rapidly by intramolecular chelate proton transfer. Accordingly their electronic spectra in the u.v.-visible region exhibit absorption bands arising from transitions within the electronic systems involved in these tautomers. **Approach:** The structures of several β -thioxoketones were geometrically optimized using B3LYP/cc-pVTZ, B3LYP/6-311++G(2d,p), PM2/6-311++G(2d,p) and B3LYP/6-311G(d,p) and their electronic spectra were theoretically calculated. TD-DFT, EOM-CCSD, CIS and semi empirical ZINDO methods were used to calculate the electronic spectra. **Results:** The spectrum of the enolic form of thiomalonaldehyde is characterized by three absorption bands at 460, 305 and 223 nm due to H \rightarrow L, H-1 \rightarrow L and both H \rightarrow L+1 and H \rightarrow L+2 transitions. The first band is attributed to n \rightarrow π^* transition within the C = S group while the others are due to transitions with the O-C = C-C = S conjugated system. Both TD-DFT and ZINDO methods were able to predict the electronic spectra of the molecules studied that are in very good agreement with the observed spectra. The observed spectra were agreed to large degree with calculated spectra of the enolic tautomer of the studied compounds. **Conclusion:** The observed spectra were agreed to large degree with calculated spectra of the enolic tautomer of the studied compounds.

Key words: Electronic spectra, electron density difference, electrostatic potential difference, theoretical program package, qualitatively similar, intramolecular chelate

INTRODUCTION

β -thioxoketones are well known compounds due to their tautomerism and in solvent spectroscopic studies had shown that they exist exclusively or preponderantly as equilibrium mixtures of the tautomeric enol (HO-CR¹=CH-CR² = S) and enethiol (HS-CR¹ = CH-CR² = O) forms, which interconvert very rapidly by intramolecular chelate proton transfer. Meanwhile, no evidence has been found for the existence of the thioxoketone tautomer (S = CR¹-CH₂-CR² = O) form (Carlasen and Duus, 1980; Jorgensen *et al.*, 1981; Saeed and Elias, 2011). The presence of strong intramolecular hydrogen bond that adjoins hydroxylic and ketonic oxygen and sulfur centers markedly stabilizes the enolic tautomers causing them to dominate over their diketo counterparts under ambient, isolated-molecule conditions (Nguyen *et al.*, 2006; Andersen *et al.*, 2000; Posokhov *et al.*, 2001) as is the

case of their structurally related analogues, β -diketones (Yamabe *et al.*, 2004; Chatterjee *et al.*, 2010). Accordingly they are of particular interest for studies of tautomerism and intramolecular hydrogen chelating properties (Gonzalez *et al.*, 1999; Gonzalez *et al.*, 1997). In this conjunction tautomeric and photochromic behavior (Hansen *et al.*, 2007; Goeski *et al.*, 2007) are among the most conducted studies on these compounds. The absorption spectra of the aromatic derivatives characterized by four absorption maxima in the u.v.-visible region, located at ca. 265, 330, 415 and 520 nm. Due to the presence of the tautomeric mixture these bands are supposed to arise from transitions involving the chromofors ArC = C, ArC = O, ArC = S, S-C = CC = O and S = CC = C-O. Thioacetylacetone exhibits two absorption bands at 296 and 355 nm. Jorgensen *et al.* (1981) were the first to investigate the electronic absorption spectra of β -thioxoketones both experimentally and theoretically. In their theoretical

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study using CNDO/S-CI procedure the enol and the enethiol tautomer were predicted to exhibit bands at 339 and 304 nm respectively. In addition they gave theoretical rationale for the substituent's effect on the absorption spectra. In the presence of much more accurate theoretical methods and programs it is important to review the electronic absorption spectra of these important compounds. In this work we investigate the electronic absorption spectra of β -thioxoketones and the rule of the substituent on them.

MATERIALS AND METHODS

The observed electronic spectra were taken from previously published works (Carlasen and Duus, 1980). The quantum chemical calculations were performed with the Firefly program. Geometrical optimizations for thiomalonaldehyde were carried out using Density Functional Theory (DFT) method at B3LYP/6-311++G(2d,p) B3LYP/cc-pVTZ and levels of theory. For all other molecules geometry optimization were done at B3LYP/6-311++G(d,p) level. B3LYP refers to the combination of functional hybrid exchange of Becke with functional correlation gradient of Lee and Yang. For the same level of theory, vibrational frequencies for all molecules were calculated to verify that the structure converged to a minimum using the zero imaginary frequencies criterion natural. Excited states were done using TD-DFT, EOM-CCSD/MP2 and CIS/MP2 methods. The semi empirical ZINDO method was employed using the ORCA theoretical program package.

RESULTS

The calculated electronic properties are shown in Fig. 1. The electronic spectra for both thione and thiol tautomers of thiomalonaldehyde at several levels of theory are gathered in Table 1. Figure 1 shows the calculated HOMO, LUMO, electron density difference and electrostatic potential difference for enol tautomer in thiomalonaldehyde. The observed and theoretically calculated electronic spectra for thioacetylacetone and thiobenzoylacetones are gathered in Table 2. Table 3 gathered the observed and theoretically calculated spectra of thiodibenzoylmethanes at TD-DFT and ZINDO methods.

DISCUSSION

Figure 1 shows the structural properties of the two most stable tautomers of thiomalonaldehyd, namely,

enol and enethiol tautomers calculated at B3LYP/6-311++G(2d,p) and B3LYP/cc-pVDZ levels of theory. The calculated energies of the enol at the two levels are -590.20841798 and -590.22854808 hartrees respectively while those for the enethiol are -590.20463800 and -590.22427322 hartrees respectively show that the enol tautomer is more stable than the enethiol. The calculated bond lengths and bond angles are apparently similar for both levels. The calculated bond lengths for the C = O groups are 1.225 and 1.226 Å at the B3LYP/cc-pVDZ and B3LYP/6-311++G(2d,p) levels are in very good agreement with that measured for hexafluoroacetylacetone by single crystal X-ray diffraction which was 1.227 Å. This gives reliability for these methods when used to study the electronic properties of such systems.

The calculated spectra of the two tautomers by the Time Dependent DFT, EOM-CCSD and CIS methods (Table 1) show that despite the three methods are agree in the main trend in that the absorption bands of the enol are at longer wavelength than the enethiol, the CIS method is in disagreement with first two methods in predicting the electronic spectra for both tautomers. The spectra will discuss on the basis of the TD-DFT results which predict three bands for them. The shortest bands at wavelengths 223 and 218 nm are of the same origin ($H \rightarrow L+1$ and $H \rightarrow L+2$) while the long and the middle bands which arise at 485 and 305 nm in the enol and at 355 and 287 nm in the enethiol are of different origins. In the enol they are $H \rightarrow L$ and $H-1 \rightarrow L$ while they $H-1 \rightarrow L$ and $H \rightarrow L$ transitions respectively. The positions (485 and 355 nm) and the oscillator strengths (0.0002 and 0.0006) of the long bands in both tautomers suggests that they are arising due to $n \rightarrow \pi^*$ transitions within the C = S and C = O chromofors.

In order to support that this band is due $n \rightarrow \pi^*$ transition in the enol tautomer, the electron density difference and the Electrostatic Potential Difference surfaces were calculated and are shown in Fig. 2. As shown in Fig. 2 the HOMO is localized to the plane of the molecule and is non-bonding molecular orbital. Meanwhile the LUMO is perpendicular to the plane of the molecule and is and is a combination of the p_z atomic orbital on the sulfur and carbon atoms. The LUMO shows relatively larger contribution on the carbon-end of the molecule and smaller contribution from the sulfur's p_z atomic orbital. On the electron density difference surface the blue color represents positive electron density difference while the red color represents negative electron density difference.

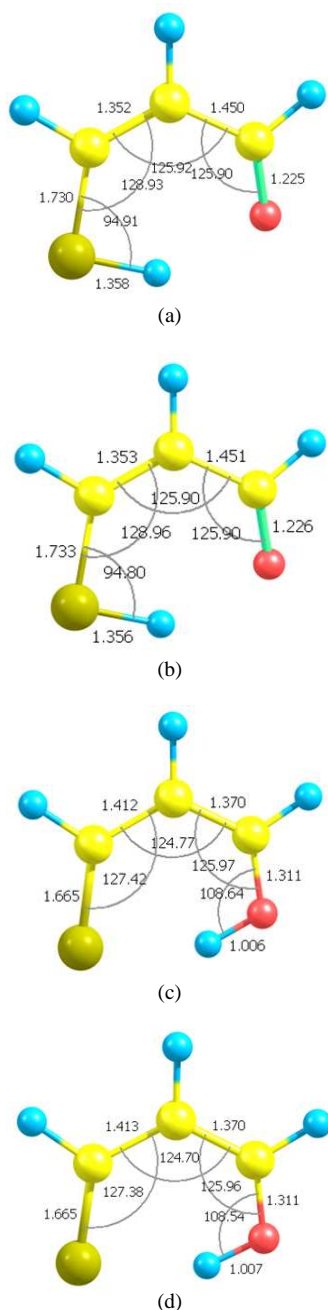


Fig. 1: The structural properties in the enol and enethiol tautomers of thiomalonaldehyde at calculated at the B3LYP/cc-pVTZ and B3LYP/6-311++G(2d,p) levels of theory (a) B3LYP/cc-pVTZ(b) B3LYP/6-311++G(2d,p) (c) B3LYP/cc-pVTZ(d) B3LYP/6-311++G(2d,p)

The electron density has increased in the $n \rightarrow \pi^*$ transition and shows a relatively large increase on the carbon atom which is furthermore, perpendicular to the

plane of the molecule. It is also clear that the negative electron density indicates that the electron density is coming from an in-plane region mainly around the sulfur atom. As electronic transition takes place the electron density will altered accordingly leading to change in the electrostatic potential. In the electrostatic potential difference surface Fig. 2 the red color means an increase in the electron density while the blue color means a decrease in the electron density. The surface gives a further indication that the electron density shifted from in-plane near the sulfur to out-of-the-plane near the carbon.

The remaining bands are due to transitions within the HO-C = C-C = S and HS-C = C-C = O conjugated systems. At the TD-DFT level the calculated bands for the enol are 485, 305 and 223 nm while those calculated for the enethiol are at 355, 287 and 218 nm. The large difference of 130 nm between the longer bands of the tautomer could be rationalize on the basis that the ionization potential of sulfur is much lower than for oxygen, which shows that the lone pair electrons on sulfur are much less firmly held than on oxygen. The relatively high energy the sulfur n orbital thus produces a bathochromic shift. The difference between the middle bands in the tautomers is much smaller (18 nm) since these bands arise due to transitions within the HO-C = C-C = S and HS-C = C-C = O systems which are of relatively comparable energies.

The theoretically calculated spectra at the DT-DFT and ZINDO methods as well as the experimental spectra for thioacetylacetone and thiobenzoylacetones are shown in Table 2. The calculated wavelengths by the two methods are in good agreement with experimental wavelengths. Both methods are able to determine the substituent effect successfully. The experimental spectrum of thioacetylacetone includes a band at 355 nm, when compared to the calculated spectra of the enol (313 nm) and enethiol (284 nm) tautomers in this compound it could be concluded that the experimental spectrum is represent that of the enol tautomer. It has been shown that substitution effect on the spectra of β -thioxoketones depends on at which side the substitution takes place. Substitution at the C=O side produces larger red shift than at C = S side Table 2. This is predicted well theoretically by both methods. According to ZINDO results Table 2 introducing a phenyl at the C = O side of thioacetylacetone shifts its calculated band by 35 (nm from 352-387 nm). The experimental shift is 34 nm only. On the other hand the experimental red shift produced at introducing a phenyl ring at the C=S side is 19 nm and the calculated shift by ZINDO method is 5 nm which show the same trend.

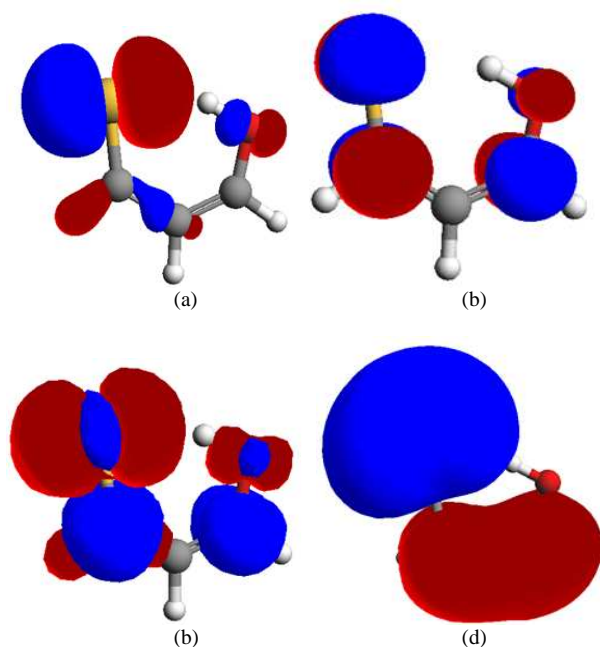


Fig. 2: HOMO, LUMO, electron density difference and electrostatic potential difference for enol tautomer (a) HOMO (b) LUMO (c) Electron density difference (d) Electrostatic potential difference

Table 1: Theoretically calculated electronic spectra of enol and enethiol tautomers at several methods using 6-311++G (2d, p) bases set

Theoretical level						
TD/B3LYP						
Tautomer	State excited	Coefficient	Oscillator strength	λ , nm	EOM-CCSD/MP2 λ , nm	CIS-MP2 λ , nm
Enol	H→L	0.70654	0.0002	485	460	356
	H-1→L	0.70089	0.2113	305	310	269
	H→L+1	0.69197	0.0238	223	201	164
	H→L+2	0.10991				
Enethiol	H-1→L	0.70237	0.0006	355	330	263
	H→L	0.69629	0.2078	287	267	230
	H→L+1	0.63058	0.0000	218	204	195
	H→L+2	0.29715				

Table 2: Observed and theoretically calculated spectra of Thioacetylacetone and thiodibenzoylaceton

Compound		TD-B3LYP/6-311++G (d, p)					
R ¹	R ²	Excited state	Coefficient	λ , nm	Oscillator strength	ZINDO λ , nm	Observed λ , nm
CH ₃	CH ₃ (thione)	H→L	0.70182	313	0.2331	352	355 ^a
CH ₃	CH ₃ (thiol)	H→L	0.63904	284	0.2117	269	---
CH ₃	Ph	H→L	0.70599	361	0.5256	387	389 ^b
Ph	CH ₃	H→L	0.67226	334	0.1517	360	374 ^b
Ph	4-MeC ₆ H ₄	H→L	0.69766	361	0.5965	389	392 ^b
Ph	4-MeOC ₆ H ₄	H→L	0.70578	362	0.5909	391	399 ^b
Ph	4-BrC ₆ H ₄	H→L	0.68307	367	0.6497	387	390 ^b

Table 3: Calculated and observed spectra of thiodibenzoylmethanes

		TD-B3LYP/6-311++G (d, p)					
R ¹	R ²	Oscillator excited state	ZINDO λ , nm	observed coefficient	strength	λ , nm	λ , nm*
Ph	Ph	H-1→L	510	0.70409	0.0001	655	515
		H→L	386	0.70044	0.4253	404	408
		H-3→L	340	0.16593	0.3045	332	325
		H-2→L	---	0.67729	---	296	262
Ph	4-BrC ₆ H ₄	H-1→L	514	0.70347	0.0001	663	520
		H→L	393	0.10023	0.5579	404	209
		H-2→L	---	0.69779	---	---	---
		H-3→L	346	0.17427	0.2864	335	328
Ph	4-MeC ₆ H ₄	H-2→L	---	0.67373	---	299	271
		H-1→L	506	0.70433	0.0001	639	515
		H→L	390	0.70013	0.4902	408	413
		H-3→L	337	0.01601	0.3018	332	323
Ph	4-MeOC ₆ H ₄	H-2→L	---	0.67815	---	295	268
		H-1→L	508	0.70415	0.0001	654	515
		H→L	390	0.69938	0.5016	408	423
		H-3→L	326	0.16562	0.2969	333	326
4-MeC ₆ H ₄	Ph	H-2→L	---	0.67706	---	296	245
		H-1→L	508	0.70004	0.0001	646	520
		H→L	385	0.68301	0.4441	403	408
		H-2→L	---	-0.10575	---	---	---
4-MeC ₆ H ₄	Ph	H-3→L	353	0.68906	0.3561	343	340
		H-2→L	---	0.10059	---	---	---

Table 3: Continue

4-MeC ₆ H ₄	4-BrC ₆ H ₄	---	---	---	---	297	261
		H-1→L	512	0.69997	0.0001	656	520
		H-2→L	392	0.13413	0.5845	403	411
		H→L		0.68884			
		H-3→L	360	0.68386	0.33	347	346
		H-2→L					
4-MeC ₆ H ₄	4-MeC ₆ H ₄	---	---	---	---	299	272
		H-1→L	504	0.70219	0.0001	640	515
		H→L	389	0.11151	0.5165	407	413
		H-2→L		0.69461			
		H-3→L	350	0.68789	0.3478	343	339
		H-2→L		-0.10706			
4-MeC ₆ H ₄	4-MeOC ₆ H ₄	---	---	---	---	296	268
		H-1→L	506	0.70212	0.0001	644	510
		H→L	389	0.12018	0.5332	406	422
		H-2→L		0.693			
		H-3→L	353	0.68619	0.3404	344	337
		H-2→L		-0.1154			
4-MeC ₆ H ₄	3-MeC ₆ H ₄	---	---	---	---	297	248
		H-1→L	510	0.70083	0.0001	651	520
		H→L	390	0.18181	0.4357	403	412
		H-2→L		0.67617			
		H-3→L	361	0.28588	0.027	344	335
		H-2→L		0.61117			
4-MeOC ₆ H ₄	Ph	---	---	---	---	300	252
		H-1→L	506	0.70382	0.0001	661	515
		H→L	385	-0.1215	0.4692	404	407
		H-2→L		0.69525			
		H-3→L	353	0.68904	0.3292	344	372
		H-2→L		0.1184			
4-MeOC ₆ H ₄	4-BrC ₆ H ₄	---	---	---	---	297	259
		H-1→L	510	0.65702	0.13061	661	520
		H→L+1		0.13061			
		H→L	328	-0.1036	0.6226	404	410
		H-2→L		0.66091			
		H-3→L	273	-0.1072	0.5986	344	368
		H-2→L		0.61475			
4-MeOC ₆ H ₄	4-MeOC ₆ H ₄	---	---	---	---	297	264
		H-1→L	503	0.6654	0.0001	649	510
		H→L	390	0.10617	0.5861	408	421
		H-2→L		0.66523			
		H-3→L	271	0.62576	0.5749	342	365
		H-2→L		0.11621			
		---	---	---	---	295	253

The electronic spectra of thiodibenzoylmethanes consist of four bands within the ranges λ_1 : 242-272, λ_2 : 323-378, λ_3 : 407- 423 and λ_4 : 510-520 nm Table 3. Theoretical calculations using the ZINDO method predicted nicely the bands λ_2 and λ_3 to be within the ranges 402-408 and 331-372 nm respectively, while it is overestimated the λ_4 band by more than 120 nm. On the other hand, TD-DFT method is predicted the bands λ_3 and λ_4 to be within the ranges 385-393 and 504-514 nm respectively. The band λ_3 which is an absorption arising alone from the O=C=C-C=S system shows shifts in consequence of variation in R². This is interpreted [] on the basis of both conjugative and inductive effects.

When R² is p-BrC₆H₅ the C = C-C = S system interacts strongly with the energetically high-lying 3p π -bromine electrons. This is true for R² = p-MeOC₆H₅,

but in the effect will be weaker due to the less effective interaction between the relatively lower lying 2p π -oxygen electrons in the methoxy group and the C = C-C = S π -system. These interactions are modified by the simultaneously operating electron-withdrawing inductive effects (Br>MeO) leading to make the net effects of the substituent are qualitatively similar.

CONCLUSION

Both TD-DFT and ZINDO methods were able to predict the electronic spectra of the molecules studied that are in very good agreement with the observed spectra. The observed spectra were agreed to large degree with calculated spectra of the enolic tautomer of the studied compounds.

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