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ORIGINAL ARTICLE

Theoretical study on the electronic spectra in cyclic 1,2-diketones

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Abstract The structural and electronic properties of some α -diketones have been investigated theoretically by performing both Hartree–Fock and density functional theory calculations at HF/6-31G(d,p) and B3LYP/6-31G(d,p) levels of theory.

The electronic spectra were calculated by ZINDO and TD methods at each level of theory. The wavelength of the $n \rightarrow \pi^*$ electronic transitions was correlated with the torsion angle between the two carbonyl groups in these compounds. The study revealed that the $n \rightarrow \pi^*$ electronic transitions in the studied compounds are functions of the torsion angles between the two carbonyl groups within the linkage CO–CO.

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1. Introduction

α -Diketones are potential building blocks in the synthesis of complex molecules (Sodeako and Hamashima, 2006). On the other hand, cyclic α -diketones are structural units in a number of biologically active compounds (Kupchan et al., 1975;

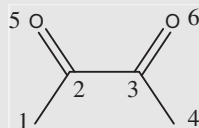
Pickels et al., 1990). This class of molecules is characterized by equilibrium between the mono-enol and di-keto forms. In smaller rings (5 and 6) they exist in the mono-enol form almost exclusively, and as the size increases the amount of di-keto form ratio increases (Cumper et al., 1965). In cyclic α -diketones that were totally substituted at the carbons adjacent to the carbonyl groups, this enol-keto equilibrium is no longer present and the di-keto is the only form present.

In α -diketones there are two lone-pair molecular orbitals and two π^* orbitals formed by the antisymmetric and symmetric combinations of the n and π^* of each carbonyl group. There are two $n \rightarrow \pi^*$ transitions of which the one between the symmetric states will strongly depend on the dihedral angle about the intercarbonyl bond. It has been demonstrated that the $n \rightarrow \pi^*$ spectra of the α -diketones depend on this torsion angle (Rao et al., 1972) and the wavelength of the electronic transition is higher when the two carbonyl groups are co-planar while it is lower for other conformations (Leonard, 1950a,b;

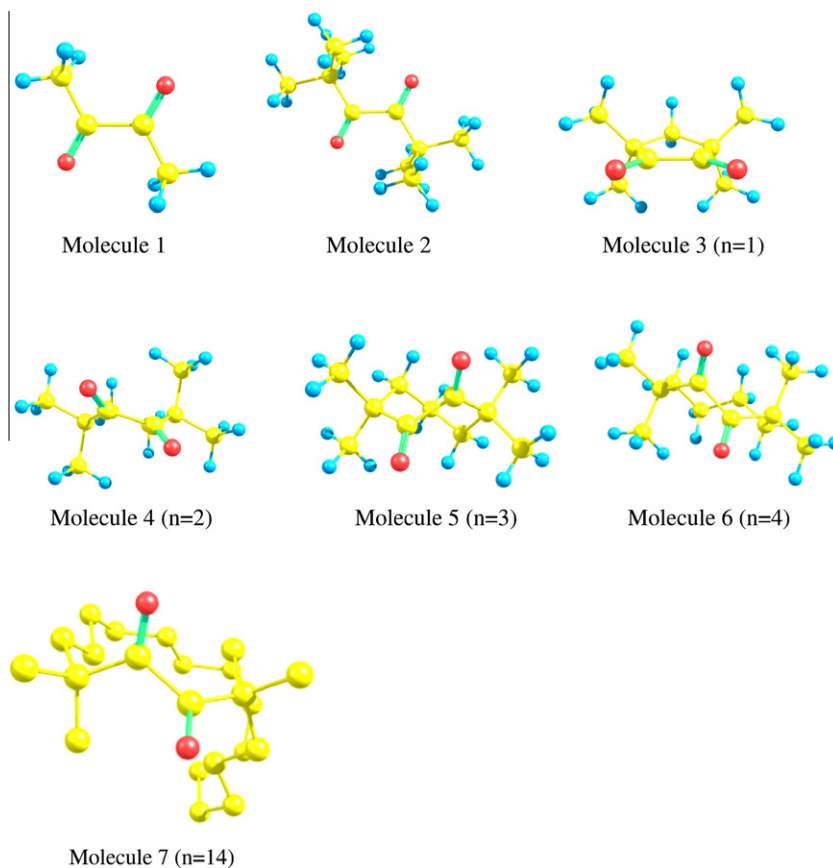
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Table 1 Some of the structural properties of the studied molecules.

Molecule	1	2	3 ($n = 1$)	4 ($n = 2$)	5 ($n = 3$)	6 ($n = 4$)	7 ($n = 14$)
<i>Bond length (Å)</i>							
C1–C2	1.508	1.541	1.529	1.532	1.5326	1.528	1.540
C2–C3	1.550	1.567	1.564	1.552	1.536	1.528	1.540
C2–O5	1.216	1.218	1.208	1.214	1.216	1.219	1.215
<i>Bond angle (°)</i>							
C1–C2–O5	124.2	121.6	129.0	124.5	124.4	123.7	121.2
C1–C2–C3	116.4	118.8	1.04.6	115.7	115.6	120.2	120.2
<i>Torsion angle (°)</i>							
O5–C2–C3–O6	180.0	180.0	0.0	49.4	85.6	106.1	109.3
<i>Atomic charge</i>							
C-1	−0.379	−0.039	−0.043	−0.047	−0.034	−0.037	−0.031
C-2	0.367	0.395	0.395	0.397	0.402	0.415	0.407
O-5	−0.417	−0.435	−0.427	−0.429	−0.452	−0.450	−0.453
Dipole moment (Deby)	0.0025	0.0005	4.652	4.359	3.533	3.069	3.316
Energy (a.u)	−306.48	−542.37	−500.63	−541.16	−580.48	−619.788	−1012.85

**Figure 1** The optimized structures of the studied molecules at B0LYP/6-01G(d,P) level. The hydrogen atoms were removed from the structure of molecule 14 for clarity.

Huang et al., 2002; Mosnacek et al., 2002; Bortolus et al., 2002).

In this work, we study the electronic spectra of α -diketones as a function of structural changes.

2. Method of calculation

The structures of the molecules were fully optimized with PCGAMESS program (Granovsky, xxxx). The resulting optimized structures and electronic properties were visualized using the program AgrusLab (Thomson, xxxx). In order to calculate the electronic transitions, the structures were first optimized at the HF/6-31G(d,p) and B3LYP/6-31G(d,p) levels of theory; then the optimized structures were used as inputs to estimate the electronic spectra using both ZINDO (Hanson et al., 1987) and TD (Bauernschmitt and Ahlrich, 1996) methods at the two levels (HF and DFT). To show CO–CO torsion angle effect on the electronic spectra of glyoxal molecule, the structures were optimized using both HF/6-31G(d,p) and B3LYP/6-31G(d,p) methods at restricted torsion angles within the range 0–180° at 15° intervals and the optimized structures

were used to estimate the spectra using both TD-HF/6-31G(d,p) and TD-B3LYP/6-31G(d,p) methods.

3. Results and discussion

Table 1 shows the total energies, some structural properties and atomic charges of the studied molecules. The optimized structure of the molecules considered (1–7) is shown in Fig. 1. It could be seen from Table 1 that the non-cyclic molecules adapted the trans geometry at the CO–CO linkage. For cyclic molecules, the torsion angle depends on the size of the aliphatic ring and increases from 0° to 109° with increasing number of the methylene groups in the ring. The calculated atomic charges for the carbon and the oxygen atoms of the carbonyl group show some dependence on the CO–CO torsion angle (Φ). The atomic charges of the carbon atom are smaller when the torsion angles are 0° or 180°, while for the oxygen atoms the charges are more negative when the two carbonyls are co-planar and less negative when they are perpendicular to each other.

Table 2 Some electronic properties of the studied compounds.

Molecule	1	2	3	4	5	6	7
HOMO (a.u)	−6.622	−6.337	−6.179	−6.178	−6.073	−6.203	−6.203
LUMO (a.u)	−2.335	−2.299	−2.232	−1.673	−0.1918	−1.289	−1.512
Electronic affinity $A = (-E_{\text{LUMO}})$	2.335	2.299	2.232	4.673	0.918	1.289	1.512
Ionization potential $I = (E_{\text{HOMO}})$	6.622	6.337	6.179	6.178	6.073	6.203	6.203
Global harness $\eta = \frac{I-A}{2}$	2.143	2.019	1.973	2.267	2.577	2.417	2.346
Electronegativity $X = \frac{I+A}{2}$	4.478	4.318	4.205	3.910	3.496	3.706	3.857
Electrophilicity $\omega = \frac{\eta^2}{2\chi}$	1.071	1.009	0.987	1.134	1.289	1.209	1.173
ΔE	4.287	4.038	3.771	4.535	5.155	4.835	4.691

Table 3 Comparison between experimental and calculated spectra of the molecules.

Molecule	Φ (°)	λ_{max} (exp)	TD	ZINDO	TD	ZINDO
1	180	450	336	493	464	493
		270	227	364	279	369
			129	197	203	197
2	180	365	346	492	497	494
		285	232	272	296	379
			136	203	217	204
3	0.0	466	364	494	514	492
		280	234	355	294	360
			145	204	221	204
4	49.9	380	316	447	416	449
		298	246	367	282	367
			145	208	243	209
5	85.6	337	266	392	345	392
		299	251	376	317	377
			141	202	221	203
6	106.1	343	281	411	377	416
		296	241	370	291	371
			143	203	231	207
7	109.3	384	298	419	392	419
		287	246	369	288	368
			147	205	232	206

Table 4 Transition energies, oscillator strengths, molecular orbital and CI coefficients of the electronic spectra of the studied molecules.

Molecule	Transition energy		Oscillator strength	Molecular orbital	CI coefficient
	cm ⁻¹	nm			
1	21562.0	460	0.0000	H → L	0.67051
	05900.9	277	0.0000	H-1 → L	0.66558
				H → L+1	-0.16296
	29257.8	200	0.0000	H-1 → L	0.17886
2	20110.9	497	0.0002	H → L+1	0.67909
				H → L	0.66284
	00786.8	296	0.0000	H → L+1	-0.14226
				H-1-L	0.66284
0	45980.7	217	0.0000	H → L+1	-0.14226
				H-5 → L	0.01058
				H-1 → L	0.19060
				H → L+1	0.59590
4	19468.4	514	0.0002	H → L	0.67809
	04012.7	294	0.0000	H-4 → L	0.11018
				H-1 → L	0.66270
				H → L-1	-0.10895
4	45261.2	221	0.0000	H-4 → L	-0.15896
				H-2 → L	0.66709
				H → L+1	-0.10522
	24019.9	416	0.0000	H → L	0.67689
4	05417.7	282	0.0000	H-1 → L	0.55656
				H → L+1	-0.08788
	41206.4	242	0.0000	H-1 → L	0.40085
				H → L+1	0.57517

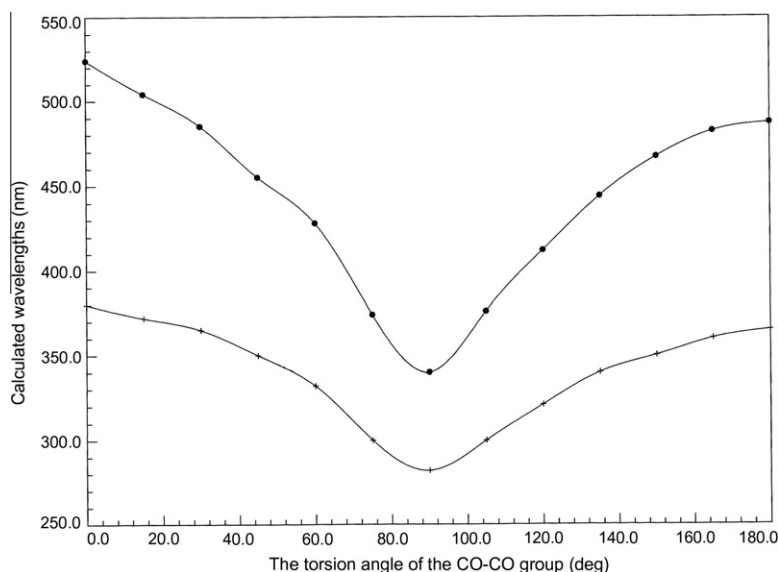
**Figure 2** Calculated wavenumbers of the long $n \rightarrow \pi^*$ transition in glyoxal versus CO-CO torsion angle. ●-●-●-●: TD-B3LYP/6-31G(d,p); +-+-+-+ : TD-HF/6-31G(d,p).

Table 2 shows the results of several molecular descriptors for the studied molecules such as electron affinity, ionization potential, global hardness, and electronegativity based on the HOMO and LUMO energies according to Koopmans theorem (Favila et al., 2007), as well as dipole moment and the inter-frontier molecular orbital energy gap (ΔE). At torsion angle near 90°, the energy gap of the system increases to maximum

due to reduced π overlap between the carbonyl groups. Since the interaction between the carbonyls is antibonding in HOMO and bonding in the LUMO, the reducing of π overlap stabilizes the HOMO level, but destabilizes the LUMO level. The degree of stabilization of the HOMO energy level is smaller in energy than the destabilization of the LUMO energy level.

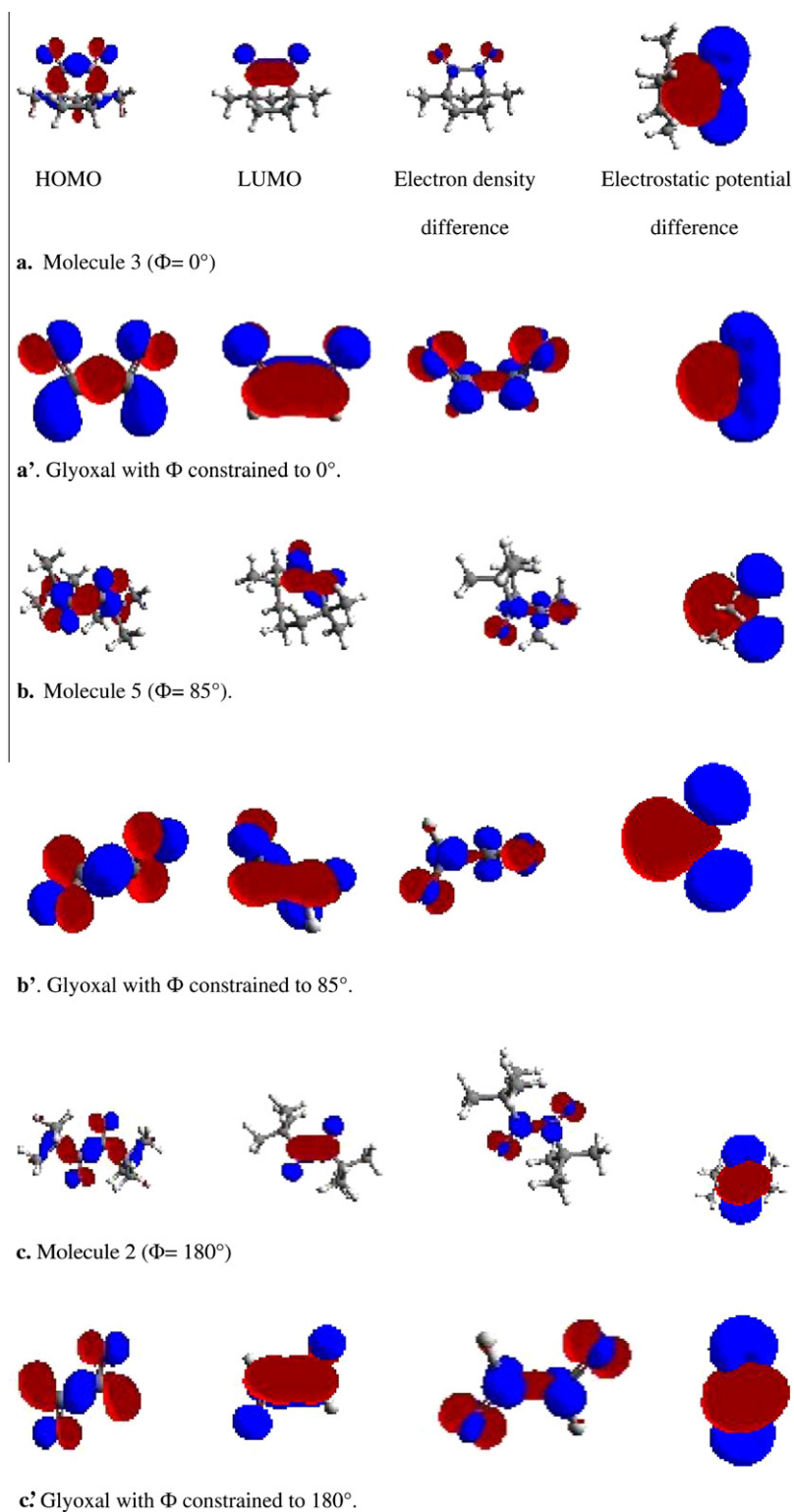


Figure 3 The electronic surfaces of some studied molecules compared to those of glyoxal constrained to the corresponding dihydal angles.

The experimental and the calculated Uv–vis spectra for the studied molecules are presented in Table 3. The TD-DFT method seems the best to estimate the electronic spectra especially for short wavelength transitions. The four methods show three spectral lines. In general, the long wavelength peak shows

a clear dependence on Φ . The wavelength changed in the direction: 553.5, 416.1, 344.8, 376.8, 391.6 and 497.2 nm when Φ changed in the direction: 0, 49.4, 85.6, 106.1, 109.3 and 180° , respectively, as calculated by TD-DFT. This is also the case in all other methods. The other spectral lines do not show this

behavior. This seems in agreement with the experimental results (Table 3). Accordingly the long wavelength line corresponds to the transition between the symmetry states in these molecules (Rao et al., 1972). In addition this line shows correlations with electronic properties gathered in Table 2. To provide insight as to the nature of electronic transitions in the studied molecules, the TD-DFT-computed singlet state excitations are presented in Table 4. From Table 4, the long wavelength transition is the $n \rightarrow \pi^*$ type arising almost exclusively from HOMO to LUMO transitions.

For glyoxal molecule, the corresponding electronic transitions are predicted for restricted Φ values ranging from 0° to 180° at 15° intervals and the results are shown in Fig. 2. The figure indicates the same trends with forgoing results in both TD-HF and TD-B3LYP methods. The transition has the highest energy at Φ values where the two carbonyls are orthogonal (less resonance) and lower values when the groups are co-planar (high resonance). To examine the first excited states in molecules, Fig. 3 shows a comparison between the HOMO, LUMO, electron density and electrostatic potential difference surfaces in molecules 3, 5 and 7 and those for glyoxal constrained to the Φ values 0° , 85° and 180° . The surfaces are similar in general for the related structures and in all cases the HOMO is localized to the plane of the molecule and is non-bonding molecular orbital. The LUMO is orthogonal to the plane of the molecule with twisted shape in the case when Φ is 85° which may explain the highest ELUMO value in the molecule 5 compared to the other molecules (Table 2). The electron density surfaces show electron density shift from an in-plane region (red color) mainly around the oxygen atoms and the intercarbonyl s Csp²-Csp² bond. This suggests that the electronic transition is dominated by a HOMO-LUMO

transition. This is further supported by the electrostatic potential difference surfaces which show the movement of the electron density from in-plane near the oxygen atoms (blue color) to out of plane (red color) near the carbon atoms within the CO-CO linkage.

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