

Theoretical molecular structure determination infrared frequencies with solvent effect of some α -diketones

ISSN -1817 -2695

Naji A.Abood, Bahjat A.Saeed and Sadiq M. Hasan Ismael

department of Chemistry, College of Education, University of Basrah

((Received 8/3/2011, Accepted 26/6/2011))

Abstract

Molecular structure determination for six α -dicarbonyl compounds as well as their vibrational frequencies have been theoretically investigated by molecular orbital by ab initio calculation based on DFT theory level using 3-21G basis set performed by B3PW91 method. Assignments for vibrational frequencies were made, and solvent effect on the IR frequencies in the carbonyl region was studied using four solvents; carbontetrachloride, chloroform, methanol and tetrahydrofuran.

α -dicarbonyl compounds exist in trans conformation with planar structure. Replacement of H atoms in glyoxal by CH₃ or phenyl groups has no effect on the planarity of the molecules. Carbon-carbon bond length of dicarbonyl moiety is shorter in dibenzoylmethane compared with glyoxal, whereas C=O bond shows opposite behavior.

The molecules have two frequencies in the carbonyl region that arise from coupling between the two carbonyl groups in the symmetrical molecules, assigned to two internal normal vibrational modes.

Keywords: Theoretical molecular structure, determination ,IR and solvent effect, α -diketones

Introduction

α -diketones have aroused considerable interest and have been attentively studied. They are interesting as intermediates in synthesis of various organic and heterocyclic compounds. Glyoxal is the simplest member of α -diketones, it exists as vapour at room temperature. IR bands of glyoxal vapour have been discussed by many researchers(1-4). Verderam et al. studied the IR and Raman spectra of solid glyoxal(5).

The accumulation of electronic and electron diffraction data have indicated that the glyoxal exists predominantly in the planar trans (C_{2h}) form(6,7), but Currie and Ramsay have found an evidence with visible electronic absorption spectrum for a small amount of the cis(C_{2v}) form(8).

Cole and Osborne have studied all IR active vibrations of glyoxal and deuterated glyoxal under resolution sufficient to determine accurately band centers from rotational structure(9). They made assignments for the vibrational spectra and proved that the glyoxal molecule is planar.

Benzil a crystalline compound, has hexagonal crystal structure(10) and possesses optical

properties(11) from which it has been named "organic quartz" since it is isomorphous with α -quartz. Benzil has been selected to various studies; Raman(12), IR(13), X-Ray diffraction (14) and Brillouin scattering(15). Colombo et al have studied IR and Raman Spectra for Benzil as a single crystal, KBr powder and in solutions. They made proposed assignments for internal fundamentals based on group frequencies for the phenyl moiety along with the polarization data for the single crystal(16).

Li et al(17) calculated the equilibrium structure of trans-glyoxal at various level of theory, Hartree-Fock, Moller-plestet second order perturbation theory density-functional theory, and the quadratic configuration-interaction singles-and-doubles (QCISD) model, using various basis sets. The empirical and also CCSD(T)/CC-PVQZ equilibrium structures are expected to be an order of magnitude more accurate than the ones from the previous calculations.

Recently, Larsen et al(18) have determined the equilibrium structure of trans-glyoxal from experimental rotational constants and calculated vibration-rotation interaction constants at the

CCSD(T)/CC-PVTZ level of theory. They found that the results are in excellent agreement with theoretical predictions at the CCSD(T)/CC-PVQZ level of theory. Tew et al(19), studied the vibrations of glyoxal using ab initio calculation that involves vibrations of large amplitude motion theory, variational theory and perturbation theory.

The aim of this work was theoretical determination of the structure, vibrational frequencies and solvent effect for some α -diketones.

Computational method

The Six α -dicarbonyl compounds studied with numbering of atoms can be represented by a general formula as shown in Fig .1

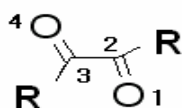


Fig 1

Where R=R=H; R=H , R=-CH₃; R=H, R=- ph; R=CH₃,R=- ph;R=R=CH₃;R=R=ph .PC Gamme program software has been used for performing ab initio calculations using DFT theory level with 3-21G basis sets. Molecular optimization was carried out, and total energies, dipole moment and bond orders have been

calculated employing B3PW91 method. IR spectrum of glyoxal in non solvent, assuming normal coordinate analysis, at the harmonic approximation, was simulated as well as for other molecules in four different solvent; CCl₄, CHCl₃, THF and methanol using PCgames program package.

Results and discussion

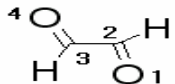
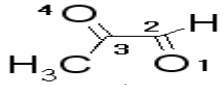
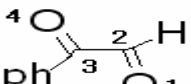
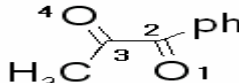
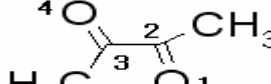
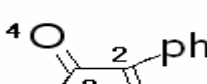
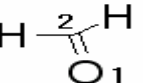
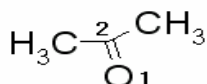
Glyoxal molecule, [H₂C₂O₂] has 6 atoms which give rise to 12 internal normal mode vibrations. The symmetry of the molecule is C_{2h} in trans form. However, the largest studied molecule is the benzil (PhCO)₂ that has 27 atoms which give rise to 72 internal normal modes of vibration since the molecule has C₂ symmetry. Therefore, the internal vibrations span the representation of 37A and 35B with both symmetry species being active in both the IR and Raman spectra.

The calculated structural parameters of the studied molecules are shown in Table 1. The C=O bond length in all the six molecules is longer than that of formaldehyde which reveals some sort of interaction between the two C=O groups. On the other hand the bond order of

C=O in acetone and formaldehyde molecules is higher than that for all the molecules studied. However, the C=O bond length in benzil is the largest among the six molecules. In addition carbon-carbon bond becomes larger in benzil molecule (1.543Å) probably due to the partial conjugation of the benzene ring with bicarbonyl moiety.

The torsional angle equals 180 degree in the six molecules which reflect the planarity of these molecules in trans conformation (the calculations in the present work). The two angles 1-2-3 and 2-3-4 are affected by substituent at carbon atom compared with that of glyoxal (Table 1).

**Table 1. Calculated, bond lengths and angles, for studied molecules.
(in Å and degree)**

No	structure	Bond length/bond order			Bond angles		
		O ₁ =C ₂	C ₂ -C ₃	C ₃ =O ₄	Torsional 1-2-3-4	1-2-3	2-3-4
1		1.229/1.852 (1.2045)*	1.515/0.784 (1.5145)*	1.229/1.852	180.00	122.16	122.12
2		1.228/1.867	1.525/0.762	1.233/1.844	180.00	123.06	118.82
3		1.229/1.838	1.527/0.792	1.243/1.738	180.00	128.01	115.09
4		1.243/1.746	1.541/0.758	1.235/1.820	179.94	116.53	123.45
5		1.234/1.848	1.540/0.877	1.233/1.840	180.00	119.15	120.36
6		1.243/1.703	1.543/0.790	1.243/1.703	180.00	119.80	119.80
7		1.227/1.930**	-----	-----	-----	-----	----- -
8		1.233/1.892**	-----	-----	-----	-----	----- --

* From ref .18

**Recalculated in this work at the same theory level and basis set

For comparison, we have calculated the total energy and dipole moment for cis and trans glyoxal using MNDO calculations, total energies -34.09182 and -34.092651 a.u ,dipole moments are 3.322 and 0.000 Debye, and heat of formations are -60.86885 and -61.38682 Kcal/mole for cis and trans conformations respectively. These facts support the existence of these compounds in the trans structure.

The values of bond order reflects the same conclusion, since the bond order of C₃=O₄ in these compounds is less than that of acetone and formaldehyde, whereas the highest value has been found in glyoxal molecule except molecule 2. The bond length C₂-C₃ connected the two carbonyl groups is 1.515Å which is the smallest value for the studied molecules in glyoxal this indicates a strong interaction between the carbonyl groups. Molecule 6 shows

the longest bond length with lowest bond order which can be attributed to a large extent of conjugation between phenyl and carbonyl groups.

The C=O bond order in these molecules is always lower than that in formaldehyde and acetone, 1.930 and 1.8890 respectively, compared with 1.852 in glyoxal (Table 1).

Benzil shows the lowest C=O bond order 1.703. The bond lengths of C=O group are always equal in the same molecule for all

symmetric studied molecules. However, the torsional angle(1-2-3-4) in these compounds is 180° which indicates that the two carbonyl groups are planar and they are taking the trans conformation. This fact is confirmed by dipole moment calculation which showed that the value of dipole moment component in z-direction equals zero, except molecule 4, and the total dipole moment value almost approaches zero in glyoxal (Table 2).

Table 2. Calculated energies and dipole moment of studied molecules (in atomic unit and debye).

No molecule	Total energy	Total potential energy	Dipole moment	X	Y	Z
1	-226.437470	-451.128020	0.000	-0.000	-0.000	0.000
2	-265.564757	-529.002123	0.869	0.752	-0.435	0.000
3	-456.165273	-908.538286	4.968	4.843	1.108	0.000
4	-495.282280	-986.401743	1.026	-1.008	-0.159	0.103
5	-304.670426	-606.861223	0.151	-0.067	-0.136	0.000
6	-685.890430	-1365.931630	0.000	-0.028	-0.000	0.000

The results of calculations of energies and dipole moments of the six molecules are listed in Table 2. Molecule 3 possesses the highest dipole moment, 4.968 Debye, whereas glyoxal and benzil molecules do not show very dipole moment as expected due to the symmetry of the molecules. However, the z-components of the dipole in all the molecules except molecule 3, are zero, which indicates the coplanarity of the molecules.

The calculated vibration frequencies for glyoxal molecule using harmonic oscillator approximation, in this work, are shown in Table 3 with assignments, and the calculated and

experimental frequencies from the literature (19,20,21).

David et al(19) used SCF-pt method including mixing of excited states through the perturbed potential with anharmonicity assumption and obtained equal results which are close to the experimental values. The vibrational modes 1 to 6 are attributed to translational and rotational motions. They are shifted in CHCl₃ to high frequencies compared with CCl₄, CH₃OH. However their values are lower than those that reported previously(19). The calculations are performed in case of solvent free the gas phase at 298K.

Table 3. Comparison of the calculated fundamental frequencies glyoxal cm^{-1} based on harmonic approximation in non solvent and some solvents with experimental values.

species	Mode no	assignment	Non solvent	solvent				Calc From ref.19	Exp from ref.20	Ref.21
				CCl_4	CHCl_3	THF	CH_3OH			
	1	(1-6) Translation and rotation	25	+0.2	+25.0	+0.6	+1.0	121	127	----
	2		11	+2.0	+7.0	+4.0	+3.0	262	252	----
	3		1	+1.7	+13.0	+10.0	+4.5	409	376	----
	4		0.8	+0.7	+3.0	+1.0	+0.5	577	498	----
	5		5	+1.0	+33.0	-3.0	-2.0	767	619	----
	6		2	+0.3	+37.0	-0.3	-1.7	987	738	----
Bu	7	C-O wag	203	+0.6	-30.0	+0.7	-3.0	262	252	----
Bu	8	C-C=O bend	315	+8.0	+31.0	+3.5	+3.0	341	339	----
Ag	9	C-C=O bend	550	-0.2	+9.0	+0.7	+2.0	548	551	----
Au	10	C-H wag	868	+2.5	-20.0	+3.0	+7.0	806	801	801.5
Ag	11	C-H stretch	1024	-2.0	+44.0	-1.4	+0.3	1035	1064	----
Bg	12	C-H wag	1118	+4.0	-23.0	+5.0	+8.0	1064	1052	----
Bu	13	C-H rock	1351	+1.0	+30.0	+8.0	+9.0	1321	1321	1312.5
Ag	14	C-H rock	1391	+1.0	+11.6	+6.0	+7.0	1353	1338	----
Bu	15	C=O str asym	1727	-4.0	-30.0	-8.0	-9.0	1765	1732	1732.1
Ag	16	C=O str sym	1736	-4.5	-9.0	-6.0	-7.0	1761	1749	----
Bu	17	C-H str sym	2974	-19.0	+18.0	+32.0	+38.0	2785	2835	----
Ag	18	C-H str sym	2991	-17.0	+18.0	+34.0	+39.0	2792	2842	----

The experimental stretching frequencies of the carbonyl groups are shifted to lower values in dideuterated glyoxal(9) (Cole) molecule which indicates sort of combination with C-H motion. Similar conclusion can be drawn for C-C=O bending, for deuterated 311 and 537 cm^{-1} compared with that of glyoxal 338 and 550 cm^{-1} from Cole data, and 315 and 550 cm^{-1} in this work.

From Table 3, stretching vibration frequency of C-H bonds, vibration modes, V17 and V18, are more affected by the nature of the solvent. They undergo blue shift in polar solvents compared with non polar solvent, CCl_4 . On the other hand, the stretching of the carbonyl groups, vibration modes, V15 and V16, are shifted to low frequency, red shift, which are expected. The other modes behave normally (Table 3).

The structures with the numbering of the atoms in studied molecules and vibrational stretching frequencies of the bicarbonyl moiety are shown in Table 4. The two frequencies in the carbonyl region for 1 and 6 molecules are arisen because of the symmetry of the two connected carbonyl groups in these molecules. The two frequencies are explained probably in terms of the coupling between the carbonyl groups and

are assigned to symmetric and asymmetric stretching vibrational motions.

On the other hand, the two frequencies in the carbonyl region for the asymmetric molecules can be individually assigned to each of the carbonyl groups. The lowest frequency can easily be assigned to vibrational of the carbonyl that is connected to phenyl ring.

The result of the calculations shows that the largest coupling among symmetric molecules is benzil molecule $\Delta\nu = 16 \text{ cm}^{-1}$ (table 4) compared with that of glyoxal molecule, $\Delta\nu = 8 \text{ cm}^{-1}$.

The calculated IR stretching frequencies for bicarbonyl moiety are shown in Table 4. The two frequencies for 1,5,6 molecules are arisen because of the symmetry of these molecules, these frequencies are preseeably due to the coupling of the two carbonyl groups. On the other hand, the two frequencies in the anti symmetric molecules can be individually assigned to each group. The lowest vibrational frequency is made presumably due to carbonyl group connected to phenyl ring. The difference between symmetric and anti symmetric vibration frequencies of the carbonyl groups in glyoxal and dideuterated glyoxal is not affected by deuteration, whereas the two frequencies are

lowered by 22 and 23 cm^{-1} respectively in deuterated glyoxal.(19).

Table 4 Vibrational stretching frequencies of bicarbonyl moiety of the Studied molecules in cm^{-1}

No	structure	$\text{C}_2=\text{O}_1$	$\text{C}_3=\text{O}_4$	$\Delta\nu$ cm^{-1}
1		1727 (1722) ^a (1732) ^b	1736 (1710) ^a (1745) ^b	9.0 (12.0) ^a (13.0) ^b
2		1736	1761	25.0
3		1746	1694	52.0
4		1689	1756	62.0
5		1748	1756	8.0
6		1697 (1680) ^c	1681 (1667) ^c	16.0 (13.0) ^c

(a) Dideuterated glyoxal from ref.9, experimental.

(b) Glyoxal from ref.9, experimental.

(c) From ref.22 .

References

- 1- A.R.H. Cole and H.W. Thomson, *proc,Roy. Soc.Ser. A*, 1949.10,200.
- 2- A.R.H. cole. *Australin. J.Sci.* 1962,25,225.
- 3- R.K. Harris, *Spectrochim. Acta* 1964,20,1129.
- 4- W.G. Fateley, R.K. Harris, F.A. Miller and R.E. Witkowski, *Spectrochim Act*, 1965,21,231.
- 5- F.D. Verderam, E.Castellucci and S.Cldano, *Chem.phys*, 1970,53,719.
- 6- F.W. Birss, J.M.Brown, A.R.H. cole, A.Lofthus, S.L.N.G. Krishna machari, G.A. Osborne, J.Paldus, D.A. Ramsay, and L. Watmann, *Can.J. Phey*, 1970,48,1230.
- 7- K.Kuchitus, T.Fukuyama and Y. Moviro, *J.Mol. Strucuter*, 1968,1,463.
- 8- G.N. Currie and D.A. Ramsay, *Can. J. Pheys*, 1971,49, 317.
- 9- A.R.H. Cole and G.A. Osborne, *Spectrochimica Acta*, 1971, 27A, 2461-2490.
- 10- E.J. Gabe, Y. Le page, F.L. Lee, L. R.C. Barclay, *Acta. Crystallography.* 1981, B37,197.
- 11- J.Jerphagon, *J. Quantum Electron*, 1971, QE-7, 42.

- 12- F. Steuman, J.Chem. Phys. 1969. 51,3141.
- 13- B. Wyncke, F. Brehat, A. Hadui, Ferroelectrics, 1980, 25, 617.
- 14- H. Tevauchi, T. Kojima, k. sakare, H. Maeda, J. Chem. Phys 1982,76,612.
- 15- A. yoshihara, E.R. Bernsteiu, J. Reich, J. Reich, J. chem.. physe, 1983, 19, 2504.
- 16- I. Colombo, D. Kirin, V. Volosek, N. E. Lind say, J.F. Sullivan and J.R. During, J.Phys. chem.. 1989, 93, 6290-6296.
- 17- K.Li, J.M. Millam and H.B. Schlegel, J. Chem. Phys, 2001, 114, 8897.
- 18- R.W. Larsen, F. Pwtowski, F. hegetund, P. Jorgenson, J. Gauss and B. Nelander, J.Phys.Chem.Chem.Phys,2003, 5,5030-5037.
- 19- David.P.Tew,N.C.Handy,S.Carter,J.Phys.Chem.Chem.Phys,2001, 3,1958-1964.
- 20- C. cossart-Magos, A. Frad and A. Tramer,Spectrochim Acta A,1975,34,195.
- 21- R.W. Larsen, F. Heqelund, J.Ceponkus and B.Nelander, J.Mol. Spectrose.2002, 211,127.
- 22- J.R. During, T.S. little, T. J. Geyer,J. Phys.Chem.,1989, 93,6296.

المستخلص

يتضمن البحث دراسة نظرية باستعمال نظرية الكثافة الالكترونية بطريقة B3PW91 وعند مستوى المجاميع الأساسية 3-21G لتراكيب بعض الجزيئات ألفا- ثنائية الكيتونات وبعض خصائصها الفيزيائية اضافة الى حسابات الترددات التذبذبية للجزيئات وتشخيص الترددات مع الاطياف العملية وكذلك دراسة تأثير المذبذبات المختلفة على ترددات تحت الحمراء للمركبات المدروسة.