Contents lists available at ScienceDirect

# Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



# Synthesis, structural elucidation and DFT studies of ortho-hydroxy acetophenones

Saikat K. Seth<sup>a,b</sup>, Dipak K. Hazra<sup>c</sup>, Monika Mukherjee<sup>c</sup>, Tanusree Kar<sup>a,\*</sup>

<sup>a</sup> Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata 700032, India

<sup>b</sup> Department of Physics, M.G. Mahavidyalaya, Bhupatinagar, Midnapore (E), West-Bengal, India

<sup>c</sup> Department of Solid State Physics, Indian Association for the Cultivation of Science, Kolkata 700032, India

### ARTICLE INFO

Article history: Received 14 July 2009 Received in revised form 10 August 2009 Accepted 15 August 2009 Available online 20 August 2009

Keywords: Acetophenone Crystal structure DFT studies HOMO-LUMO energies

#### ABSTRACT

Two ortho-hydroxy acetophenones, namely 2,6-dihydroxy-4-methyl acetophenone  $[C_9H_{10}O_3]$  (1) and 2,4-dihydroxy-3-acetyl-6-methyl acetophenone  $[C_{11}H_{12}O_4]$  (2) have been synthesized and characterized by spectroscopic and X-ray structural studies. Compound (1) crystallizes in monoclinic system, space group P21/c, with *a* = 3.888(3) Å, *b* = 26.974(17) Å, *c* = 14.940(9) Å,  $\beta$  = 91.919(8)°, Z = 8, whereas compound (2) crystallizes in orthorhombic system, space group Pbca, with *a* = 7.255(2) Å, *b* = 14.410(4) Å, *c* = 18.332(1) Å, *Z* = 8. The crystal packing of (1) exhibits intermolecular O–H…O hydrogen bonds forming a parallel chain propagating along (0 1 0) direction, whereas in (2), the combination of intermolecular C–H…O hydrogen bonds and  $\pi$ - $\pi$  interactions generate a two-dimensional network. The molecular geometries and electronic structure of (1) and (2) were calculated at the DFT level using the hybrid exchange correlation functional, BLYP, PW91, PBE and BP.

© 2009 Elsevier B.V. All rights reserved.

# 1. Introduction

Self assembly is the fundamental molecular recognition process adopted by nature to generate the elegant and intricate molecular machinery from which life is built. Appropriate complementarities between the substrate and the substituting group are the necessary prerequisite for molecular recognition. The properties of crystalline material strongly depend on how the constituent components are organized with respect to one another and a control over this organization directly provides a handle over the functional properties of the material. Crystals are assembled in spontaneous process called self-assembly that proceeds through a series of molecular recognition events. Identification of robust recognition motif or a pattern of recognition is at the heart of gaining a control over the self-assembly process. A recognition event between a set of molecular components is the outcome of the mutual interaction through various forces that is in operation. Hydrogen bonding still remains the most reliable and widely used means of enforcing molecular recognition [1–3] of crystalline materials, other weaker forces such as  $\pi - \pi$  [4–7] forces associated with aromatic- $\pi$  systems have also been successfully utilized in this regard. Over the years much effort has been concentrated on characterization of hydrogen bonded systems in order to provide parameters to describe hydrogen bond strength and geometry [8-13]. The investigations in hydrogen bonding of ortho-hydroxy acetophenones [14–19] proved that the greatest steric impact of a substituent on the hydrogen bridge length is with substitution at the phenyl ring of the ortho-hydroxy acetophenones. As part of our ongoing studies to elucidate the relationships between the characteristics of the functional dyes containing acetophenone skeletons and their molecular structures and to investigate the possibilities for interand intramolecular hydrogen bonding in the solid state, the Xray structure analyses were undertaken. In this paper we report synthesis, spectroscopic characterization, crystal structures determination and hydrogen bonding of 2,4-dihydroxy-4-methyl acetophenone (1) and 2,4-dihydroxy-3-acetyl-6-methyl acetophenone (2) along with the DFT calculations to investigate the molecular geometry and electronic structure.

# 2. Experimental

#### 2.1. Synthesis

A mixture of orcinol (1.00 gm, 0.0074 mol) and glacial acetic acid (15 ml) was stirred at 0 °C with subsequent addition of boron trifluoride etherate (7.54 ml, 0.0592 mol) following by stirring at room temperature for 48 h. The reaction mixture was cooled and most of acetic acid was distilled out under reduced pressure. The mixture was then quenched with sodium-bicarbonate solution and extracted with ( $3 \times 20$ ) ml of chloroform. The organic layer was separated and dried under anhydrous sodium sulphate. Then the organic layer was concentrated. The product was purified with silica gel chromatography. Elution with petroleum-ether:ethyl acetate (5:1) furnished the required compound (1) and further elution with the same in the ratio (11:50) furnished compound (2).

<sup>\*</sup> Corresponding author. Fax: +91 33 2473 2805. *E-mail address:* mstk@iacs.res.in (T. Kar).

<sup>0022-2860/\$ -</sup> see front matter @ 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2009.08.013

Table 2

calculations for the title compounds.

Compound (1)

*Compound* (1): NMR data exists in the literature [20].

Compound (2): <sup>1</sup>H NMR (300 MH<sub>Z</sub>, CDCl<sub>3</sub>):  $\delta$  2.58 (S, 3H), 2.66(S, 3H), 2.75 (S, 3H), 6.30 (S, 1H), 14.2 (S, 1H) (for intra molecular H-bonding), 15.74 (for intermolecular hydrogen bonding); <sup>13</sup>C NMR (75 MH<sub>7</sub>, CDCl<sub>3</sub>): δ 25.9, 33.0, 33.6, 109.1, 113.4, 113.4, 149.15, 169.2, 170.5, 204.3, 205.6.

# 2.2. Crystallographic analysis

Single crystal X-ray diffraction intensity data of the title compounds were collected at 150(2) K using a Bruker APEX-II CCD diffractometer equipped with graphite monochromated  $M_{0}$  K $\alpha$ radiation ( $\lambda$  = 0.71073 Å). Data red the program Bruker SAINT [21]. the absorption coefficients, no a plied. The structures of both the compounds were solved by direct methods and refined by the full-matrix least-square technique on  $F^2$  with anisotropic thermal parameters to describe the thermal motions of all non hydrogen atoms using the programs SHELXS97 and SHELXL97 [22], respectively. All hydrogen atoms were located from difference Fourier map and treated as riding. A summary of crystal data and relevant refinement parameters are given in Table 1. Selected bond lengths and angles of compounds (1) and (2) are given in Table 2.

# 2.3. Computational

The isolated molecule DFT calculations were carried out using DMol<sup>3</sup> code [23] of the Materials studio of system of programs in the framework of a generalized-gradient approximation (GGA) [24]. The starting atomic coordinates were taken from the final X-ray refinement cycle. The geometry of the molecules was fully optimized using the hybrid exchange-correlation functional BLYP [25,26], PW91 [27], PBE [24] and BP [28,29] with a double numeric plus polarization (DNP) basis set. The electronic structures were calculated at the same level. No constraints to bonds, angles or dihedral angles were applied in the calculations, and all atoms were free to optimize. Convergence in the calculations was assumed to be reached when the total energy change between two

# Table 1

Crystal data and structure refinement parameters for  $C_9H_{10}O_3$  (1) and  $C_{11}H_{12}O_4$  (2).

ductions were carried out using	03-C8	1.2
Because of very small values of	C3-C10	-
hearntion corrections were an-	C10-C11	-
ibsorption corrections were ap-	04-C10	-

Bond lengths(Moiety A)(Moiety B) $C2-C3$ 1.383(5)1.386(5)1.4081.432(2)1.444 $C3-C4$ 1.374(5)1.378(5)1.3951.431(2)1.453 $C4-C5$ 1.426(5)1.415(5)1.4271.420(2)1.430 $C5-C6$ 1.431(5)1.417(5)1.4431.414(2)1.430 $C5-C8$ 1.452(5)1.465(5)1.4741.470(2)1.476 $C8-C9$ 1.479(5)1.491(5)1.5161.492(2)1.511 $O1-C4$ 1.356(4)1.361(4)1.3841.328(2)1.335 $O2-C6$ 1.342(4)1.357(4)1.3491.340(2)1.338 $O3-C8$ 1.258(4)1.255(4)1.2601.247(2)1.263 $C3-C10$ 1.466(2)1.467 $C10-C11$ 1.500(2)1.520 $O4-C10$ 1.500(2)1.520 $O4-C10$ 1.500(2)1.520 $C6-C5-C8$ 120.2(4)123.8(4)123.02123.3(1)123.77 $C6-C5-C8$ 120.2(4)119.7(3)118.70119.2(1)118.36 $C2-C3-C4$ 121.3(4)123.02123.3(1)123.77 $C6-C5-C6$ 121.4(4)121.3(3)121.82122.4(1)122.49 $C4-C5-C6$ 115.9(3)116.0(3)115.97116.6(1)116.95 $C5-C6-C7$ 121.3(4)122.3(4)121.39121.5(1)120.84 $O1-C4-C5$ 117.9(3)116.0(3)115.971		X-ray		DFI(BLYP)	X-ray	DFI(BLYP)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Bond lengths	(Moiety A)	(Moiety B)			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C2-C3	1.383(5)	1.386(5)	1.408	1.432(2)	1.444
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C3-C4	1.374(5)	1.378(5)	1.395	1.431(2)	1.453
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4-C5	1.426(5)	1.415(5)	1.427	1.420(2)	1.430
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C5-C6	1.431(5)	1.417(5)	1.443	1.414(2)	1.430
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	C5–C8	1.452(5)	1.465(5)	1.474	1.470(2)	1.476
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C8-C9	1.479(5)	1.491(5)	1.516	1.492(2)	1.511
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	01-C4	1.356(4)	1.361(4)	1.384	1.328(2)	1.335
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	02-C6	1.342(4)	1.357(4)	1.349	1.340(2)	1.338
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O3-C8	1.258(4)	1.255(4)	1.260	1.247(2)	1.263
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C3-C10	-	-	-	1.466(2)	1.467
O4-C10 - - - 1.254(2) 1.271   Bond angles   123.8(4) 123.02 123.3(1) 123.77   C5-C8-C9 124.3(4) 123.8(4) 123.02 123.3(1) 123.77   C6-C5-C8 120.2(4) 119.7(3) 118.70 119.2(1) 118.36   C2-C3-C4 121.3(4) 121.2(4) 120.97 117.8(1) 117.46   C3-C4-C5 121.4(4) 121.3(3) 121.82 122.4(1) 122.49   C4-C5-C6 115.9(3) 116.0(3) 115.97 116.6(1) 116.95   C5-C6-C7 121.3(4) 122.3(4) 121.39 121.5(1) 120.84   O1-C4-C3 120.7(4) 120.8(3) 119.55 120.4(1) 119.75   O1-C4-C5 117.9(3) 117.9(3) 117.8(3) 117.77   O2-C6-C7 117.7(4) 117.6(3) 117.27 117.1(1) 117.27   O3-C8-C5 119.1(3) 119.3(3) 119.94 119.1(1) 119.24   O4-C	C10-C11	-	-	-	1.500(2)	1.520
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	04-C10	-	-	-	1.254(2)	1.271
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Bond angles					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C5-C8-C9	124.3(4)	123.8(4)	123.02	123.3(1)	123.77
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C6-C5-C8	120.2(4)	119.7(3)	118.70	119.2(1)	118.36
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C2-C3-C4	121.3(4)	121.2(4)	120.97	117.8(1)	117.46
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C3-C4-C5	121.4(4)	121.3(3)	121.82	122.4(1)	122.49
C5-C6-C7121.3(4)122.3(4)121.39121.5(1)120.84O1-C4-C3120.7(4)120.8(3)119.55120.4(1)119.75O1-C4-C5117.9(3)117.9(3)118.63117.3(1)117.77O2-C6-C7117.7(4)117.6(3)117.27117.1(1)117.27O3-C8-C5119.1(3)119.3(3)119.94119.1(1)119.24O4-C10-C3120.0(1)120.62O4-C10-C11115.1(1)114.37	C4-C5-C6	115.9(3)	116.0(3)	115.97	116.6(1)	116.95
01-C4-C3 120.7(4) 120.8(3) 119.55 120.4(1) 119.75   01-C4-C5 117.9(3) 117.9(3) 118.63 117.3(1) 117.77   02-C6-C7 117.7(4) 117.6(3) 117.27 117.1(1) 117.27   03-C8-C5 119.1(3) 119.3(3) 119.94 119.1(1) 119.24   04-C10-C3 - - - 120.0(1) 120.62   04-C10-C11 - - - 115.1(1) 114.37	C5-C6-C7	121.3(4)	122.3(4)	121.39	121.5(1)	120.84
01-C4-C5 117.9(3) 117.9(3) 118.63 117.3(1) 117.77   02-C6-C7 117.7(4) 117.6(3) 117.27 117.1(1) 117.27   03-C8-C5 119.1(3) 119.3(3) 119.94 119.1(1) 119.24   04-C10-C3 - - - 120.0(1) 120.62   04-C10-C11 - - - 115.1(1) 114.37	01-C4-C3	120.7(4)	120.8(3)	119.55	120.4(1)	119.75
02-C6-C7 117.7(4) 117.6(3) 117.27 117.1(1) 117.27   03-C8-C5 119.1(3) 119.3(3) 119.94 119.1(1) 119.24   04-C10-C3 - - - 120.0(1) 120.62   04-C10-C11 - - - 115.1(1) 114.37	01-C4-C5	117.9(3)	117.9(3)	118.63	117.3(1)	117.77
O3-C8-C5 119.1(3) 119.3(3) 119.94 119.1(1) 119.24   O4-C10-C3 - - - 120.0(1) 120.62   O4-C10-C11 - - - 115.1(1) 114.37	02-C6-C7	117.7(4)	117.6(3)	117.27	117.1(1)	117.27
04-C10-C3 120.0(1) 120.62 04-C10-C11 115.1(1) 114.37	03-C8-C5	119.1(3)	119.3(3)	119.94	119.1(1)	119.24
04-C10-C11 115.1(1) 114.37	04-C10-C3	-	-	-	120.0(1)	120.62
	04-C10-C11	-	-	-	115.1(1)	114.37

Selected bond lengths (Å), bond angles (°) determined by X-ray diffraction and DFT

Compound (2)

consecutive self-consistent field (SCF) cycles was less than  $1 \times 10^{-5}$  a.u.

# 3. Results and discussion

#### 3.1. Structural description

The molecular views [30] of (1) and (2) with atom numbering scheme are shown in Figs. 1 and 2, respectively. There are two

	(1)	(2)
Empirical formula Formula weight	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub> 166.17	C <sub>11</sub> H <sub>12</sub> O <sub>4</sub> 208.21
Temperature (K)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, P2 <sub>1</sub> /c	Orthorhombic, Pbca
a, b, c (Å)	3.888(3), 26.974(17), 14.940(9)	7.255(2), 14.410(4), 18.332(1)
α, β, γ (°)	90.0, 91.919(8), 90.0	90.0, 90.0, 90.0
Volume (Å <sup>3</sup> )	1566.0(17)	1916.5(8)
Ζ	8	8
Density (calc.) (Mg/m <sup>3</sup> )	1.410	1.443
Absorption coefficient (mm <sup>-1</sup> )	0.106	0.110
F(000)	704	880
Crystal size (mm <sup>3</sup> )	0.18  imes 0.10  imes 0.08	$0.28 \times 0.24 \times 0.18$
Limiting indices	_3<=h<=3, _25<=k<=25, _14<=l<=14	_8<=h<=8,_17<=k<=17,_21<=l<=21
Reflections collected/unique	8537/1383 [R(int) = 0.0683]	16710/1689 [R(int) = 0.0298]
Completeness to $\theta$ (%)	100.0	100.0
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	1383/0/227	1689/0/141
Goodness-of – fit on $F^2$	1.038	1.067
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0463, \ wR_2 = 0.1145$	$R_1 = 0.0344, wR_2 = 0.0969$
R indices (all data)	$R_1 = 0.0621, wR_2 = 0.1255$	$R_1 = 0.0397, wR_2 = 0.1030$
Largest diff. peak and hole $(e^{A^{-3}})$	0.245 and -0.223	0.218 and -0.232

 $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ ,  $wR_2 = [\sum \{(F_0^2 - F_c^{-2})^2] / \sum \{w(F_0^{-2})^2\}|^{1/2}$ ,  $w = 1/\{\sigma^2(F_0^2) + (aP)^2 + bP\}$ , where a = 0.0838P and b = 0.0000 for (1) and a = 0.0552P and b = 0.7062 for (2).  $P = (\overline{F_0}^2 + 2F_c^2)/3$  for both the structures.



Fig. 1. An ORTEP view and atom numbering scheme of molecule (1) with displacement ellipsoids at the 30% probability level.



**Fig. 2.** An ORTEP view and atom numbering scheme of molecule (2) with displacement ellipsoids at the 30% probability level.

molecules in the independent part of the unit cell in (1) but compound (2), consists one independent molecule in the unit cell. There are only minor differences in geometrical parameters of the two independent moieties A and B in (1) (Table 2). These molecules in the asymmetric unit are almost flat. The angle between the best planes of both (acyl and aromatic) fragment in (1) are  $2.71(12)^{\circ}$  and  $1.79(13)^{\circ}$  for moiety A and B, respectively. In (2), the acyl group which is ortho to both the hydroxyl goup and ortho to methyl group forms angles 4.76(5)° and 2.51(4)° with the aromatic ring. The intramolecular geometry of the title compounds are dominated by hydrogen bond involving the hydroxyl groups and the oxygen atom of the carbonyl groups. Experimental observation gives the shortest distances between the oxygen molecules are 2.475(4) Å in (1) and 2.417(1) Å in (2), which are relatively strong and almost coplanar with the aromatic rings. In (1), the planarity of the hydrogen bonded molecular fragment passing through the hydrogen bond O2B-H2B-O3B is largely deviated from the least square mean planes of the aromatic ring by  $1.79(1)^{\circ}$  and that for (2) is  $2.40(3)^{\circ}$  for O1-H1...O4 hydrogen bond.

Intramolecular hydrogen bonding has little effect on the C–O bond lengths [C6A–O2A, C6B–O2B, C6–O2, C4–O1] of the partici-



Fig. 3. Generation of 1-D infinite parallel chain propagating along [0 1 0] direction in compound (1). The hydrogen atoms not involve in hydrogen bonding shown as broken off bonds.

#### Table 3

Hydrogen bonding geometry of  $C_9H_{10}O_3$  (1) and  $C_{11}H_{12}O_4$  (2) (Å, °).

D–H…A	d(D-H)	$d(H \cdots A)$	d(D…A)	D–H…A
Compound <b>1</b>				
02B-H2B-03B	0.82	1.74	2.475(4)	148.0
02A-H2A03A	0.82	1.78	2.508(4)	147.0
01B-H1B…03A <sup>(i)</sup>	0.82	1.93	2.734(4)	166.0
01A-H1A…02B <sup>(ii)</sup>	0.82	1.96	2.765(4)	166.0
Compound <b>2</b>				
01-H1…04	0.82	1.67	2.417(1)	150.0
02-H203	0.82	1.75	2.488(1)	147.0
C11-H11AO4 <sup>(iii)</sup>	0.96	2.58	3.530(2)	170.0
$Cg(1)\cdots Cg(1)^{(iv)}$			3.632(7)	

Cg(1) is the centroid of (C2-C7) ring.

Symmetry codes: (i) x - 1, y, z; (ii) 1 - x,  $-\frac{1}{2} + y$ ,  $\frac{1}{2} - z$ ; (iii) 1 - x, -y, 2 - z; (iv)  $\frac{1}{2} + x$ , y,  $\frac{3}{2} - z$ .

pating phenol group of (1) and (2). The C–O bond distances lying in the range 1.342(4)-1.361(4) Å in (1) and 1.328(2)-1.340(2) Å in (2) (Table 2) are similar to those found in analogous structures. These bond distances do not vary significantly despite the differing intermolecular interaction patterns observed in various compounds [19,31–35]. Due to involvement in hydrogen bonding also the carbonyl C=O bonds lengths [1.255(4)-1.258(4)Å in (1) and 1.247(2)-1.254(2)Å in (2)] are somewhat longer than those reported earlier [32,36] but agree well with [31,33,37]. The bond lengths of the benzene ring of both compounds are distorted: those flanking the carbonyl group, C5A–C4A, C5A–C6A, C5B–C4B, C5B– C6B in (1) and C5–C4, C5–C6, C3–C2, C3–C4 in (2) are in the range 1.414(2)-1.432(2)Å, whereas the others lie between 1.374(2)-1.390(2)Å (Table 2).

The crystal structures adopted by (1) and (2) are quite different. The structure of (1) includes a combination of intra and intermolecular O-H…O hydrogen bonding interactions. It is convenient to consider the substructures generated by each type hydrogen bonds acting individually, and then the combination of the substructures to build a framework. In (1), the hydroxyl O1A atom in the molecule at (x, y, z) acts as a donor to O2B atom in the molecule at  $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$  and another carboxyl atom O1B atom in the molecule acts as a donor to the carbonyl O3A atom of acetyl group in the molecule at (x - 1, y, z), so generating an infinite parallel one-dimensional chain propagating along [0 1 0] direction. Similar molecular recognition have been noticed before [31,34,35] where the organization of molecules displays parallel chain. Since O1A, O3A atoms are in molecule 'A' and O1B, O2B atoms in molecule 'B', the molecular packing contain almost parallel molecules with alternating ABABAB… chains which stacks parallel to b-axis (Fig. 3).

The molecules of compound (2) are linked by C–H…O and  $\pi$ – $\pi$ stacking interactions (Table 3). The formation of molecular framework can be readily analyzed in terms of one-dimensional substructures. In the first substructure the methyl C11 atom of acetyl group in the molecule at (x, y, z) acts as hydrogen bond donor to carbonyl O4 atom in the molecule at (1 - x, -y, 2 - z), generating a centrosymmetric  $R_2^2(8)$  ring. In another substructure, the molecules are interacting through  $\pi$ - $\pi$  stacking interactions. The phenyl rings C2–C7 of the molecules at (x, y, z) are in contact with the partner molecule at  $(\frac{1}{2} + x, y, \frac{3}{2} - z)$  with a ring centroid separation of 3.6322(7) Å, The combination of two type of substructures generated through C–H…O hydrogen bonds and  $\pi$ – $\pi$ interactions results in a two-dimensional supramolecular framework in (2) (Fig. 4). This dual recognition induced self-assembly of the monomeric units has been observed in the literature [16,31,33,37], where it has been found that the  $\pi$ - $\pi$  stacking interactions with other weak dipolar interactions are responsible for the formation of molecular self-assembly. However this  $\pi$ - $\pi$  stacking interaction has not been thoroughly explored so far as a routine tool in the design and construction of self-assembled structures.



**Fig. 4.** Monomeric units of (2) link one another by self-complementary C11-H11A···O4 hydrogen bonds and  $\pi$ - $\pi$  stacking interactions leading to the formation of 2-D assembly.



**Fig. 5.** (a) Superposition of molecular conformations obtained from X-ray analysis (blue and green), and DFT calculation (red) of compound (1). (b) Total electronic charge density isosurface of compound (1) set at 0.15 eÅ<sup>-3</sup> using DFT method. (c) Charge density of HOMO orbital of the compound (1) calculated by DFT method. (d) Charge density of LUMO orbital of the compound (1) calculated by DFT method. (For interpretation of colour mentioned in this figure, the reader is referred to the web version of this article.)



**Fig. 6.** (a) Superposition of molecular conformations obtained from X-ray analysis (blue), and DFT calculation (red) of compound (**2**). (b) Total electronic charge density isosurface of compound (**2**) set at 0.15 eÅ<sup>-3</sup> using DFT method. (c) Charge density of HOMO orbital of the compound (**2**) calculated by DFT method. (d) Charge density of LUMO orbital of the compound (**2**) calculated by DFT method. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

#### 3.2. Geometry and electronic structure

A superposition of the molecular conformations of (1) and (2) as established by the quantum mechanical calculations and X-ray studies show an excellent agreement (Figs. 5a and 6a). Since the resulting molecular geometry depends on the choice of functionals, theoretical calculations were carried out with the BLYP [25,26], PW91 [27], PBE [24], and BP [28,29] levels of theory using the numeric DNP basis set. Different functionals describe different classes of molecules with varying degrees of accuracy. Between the four functionals used for the DFT calculation, the results with the BLYP functional agree more closely with the X-ray analysis of the title compounds. The largest deviation of the geometrically optimized bond lengths/angles from the corresponding experimental values is 0.037 Å for C–C and 1.5° for C–C–C for both the compounds (Table 2). The small differences between the calculated and observed geometrical parameters can be attributed to the fact that the theoretical calculations were carried out with isolated molecules in the gaseous phase, whereas the experimental values were based on molecules in the crystalline state. All oxygen atoms in both compounds bear negative charges. The carbon atoms of the phenyl ring (C2, C4, and C6), and C8 of acyl group in (1) and in (2), phenyl ring (C2, C4, and C6), and C8, C10 of acyl group bear positive charges; the remaining carbon atoms of the phenyl rings bear negative charges. The large electron densities at the carbonyl O atom (O3) in (1) and (O3, O4) in (2) suggests possible protonation. The net charges of atoms and the molecular orbital energy of compound (1) and (2) calculated at the BLYP level are listed in Table S1 (Supplementary). The total electronic charge density isosurface, set at 0.15 eÅ<sup>-3</sup> for an isolated molecule for both compounds (Figs. 5b and 6b), indicates that charge density are equally distributed in over the entire molecules.

The charge densities for the HOMO and LUMO in (1) and (2) are shown in Figs. 5(c and d) and 6(c and d), respectively. The orbital energy level analysis for both compounds at the BLYP level shows  $E_{\text{HOMO}}$  (highest occupied molecular orbital) and  $E_{\text{LUMO}}$  (lowest unoccupied molecular orbital) values of -5.254 eV, -2.337 eV in (1) and -5.688 eV, -2.698 eV in (2), respectively. The magnitude of the HOMO–LUMO energy separation could indicate the reactivity pattern of the molecule [38].

## 4. Conclusion

The molecular conformations of two acetophenone (1) and (2) have been established by single crystal X-ray diffraction and the quantum mechanical calculations. The molecular geometry and the electronic structure have been analyzed by the DFT calculations, the results with the BLYP functional agree more closely with the X-ray analysis of the title compounds.

# Acknowledgements

S.K. Seth is grateful to the DST-funded National Single Crystal X-ray Diffraction facility at the Department of Inorganic Chemistry, IACS, India for data collection. The authors thank Debayan Sarkar, Department of organic chemistry, Indian Association for the Cultivation of Science for his interest, help and stimulating discussions.

#### Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 732688 and 732689 of compounds (1) and (2), respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, CambridgeCB2 1EZ, UK. Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2009.08.013.

#### References

- [1] Y. Zhang, Z. Yang, F. Yuan, H. Gu, P. Gao, B. Xu, J. Am. Chem. Soc. 126 (2004) 15028.
- [2] G.A. Jeffrey, An Introduction to Hydrogen Bonding, Oxford University Press, Oxford, 1997.
- [3] G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond in Structural Chemistry and Biology, Oxford University Press, Oxford, 1999.
- [4] C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885.
- [5] A.P. Bisson, F.J. Carver, D.S. Eggleston, R.C. Haltiwanger, C.A. Hunter, D.L. Livingstone, J.F. McCabe, C. Rotger, A.E. Rowan, J. Am. Chem. Soc. 122 (2000) 8856.
- [6] V. Berl, I. Huc, R.G. Khoury, M.J. Krische, J.-M. Lehn, Nature 407 (2000) 720.
- [7] W.N. Alcock, P.R. Barker, J.M. Haider, M.J. Hannon, C.L. Painting, Z. Pikramenou, F.A. Plummer, K. Rissanen, P. Saarenketo, Dalton Trans. (2000) 1447
- [8] G. Gilli, F. Berthlucci, V. Ferretti, V. Bertolasi, J. Am. Chem. Soc. 111 (1989) 1023.
- [9] G. Gilli, V. Bertolasi, in: Z. Rappoport, S. Patai (Eds.), The Chemistry of Enols, Wiley, Chichester, 1990.
- [10] P. Gilli, V. Ferretti, V. Bertolasi, G. Gilli, Adv. Mol. Struct, Res. 2 (1996) 67.
- [11] P.E. Hansen, R. Kawecki, A. Krowcsynski, L. Kozerski, Acta Chem. Scand. 44 (1990) 826.
- [12] H. Lampert, W. Mikenda, A. Karpfen, J. Phys. Chem. 100 (1996) 1718.
- [13] K.B. Borisenko, C.W. Bock, I. Hargittai, J. Phys. Chem. 100 (1996) 7426.
- [14] J. Abildgaard, S. Bolvig, P.E. Hansen, J. Am. Chem. Soc. 120 (1998) 9063.
- [15] M. West-Nielsen, P.M. Dominiak, K. Wozniak, P.E. Hansen, J. Mol. Struct. 789 (2006) 81.
- [16] A. Filarowski, A. Kochel, A. Koll, G. Bator, S. Mukherjee, J. Mol. Struct. 785 (2006) 7.
- [17] A. Filarowski, A. Kochel, Phys. Org. Chem. 18 (2005) 986.
- [18] A. Filarowski, A. Koll, A. Kochel, J. Kalenik, P.E. Hansen, J. Mol. Struct. 700 (2004) 67.
- [19] A. Filarowski, A. Kochel, P.E. Hansen, A. Urbanowich, K. Szymborska, J. Mol. Struct. 844–845 (2007) 77.
- [20] P.E. Hansen, M. Christoffersen, S. Bolvig, Magn. Reson. Chem 31 (1993) 893.
- [21] Bruker, SAINT (Version 6.36a) Bruker AXS Inc., Madison, Wisconsin, USA, 2002.
- [22] G.M. Sheldrick, SHELXS97 and SHELXL97: Programs for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997.
- [23] B. Delley, Phys. Rev. B 66 (2002) 155125.
- [24] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [25] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
- [26] A.C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [27] J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.
- [28] D. Becke, Phys. Rev. A 38 (1988) 3098.
- [29] J.P. Perdew, Phys.Rev. B 33 (1986) 8822.
- [30] L.J. Farrugia, ORTEP III (Version 1.06), Department of Chemistry, University of Glasgow, Scotland, UK, 1997.
- [31] P.E. Hansen, S. Bolvig, K. Wozniak, J. Mol. Struct. 749 (2005) 155.
- [32] A.J. Kresge, A.J. Lough, Y. Zhu, Acta Cryst. E 58 (2002) 01057.
- [33] M.G. Soares, A.P.V.D. Felippe, E.F. Guimaraes, M.J. Kato, J. Ellena, A.C. Doriguetto, J. Braz. Chem. Soc. 17 (2006) 1205.
- [34] S.Y. Li, J.F. Wang, Z.H. Zheng, Q.Y. Xu, Y.J. Huang, Y.F. Zhao, W.J. Su, Acta Cryst. E 59 (2003) 01469.
- [35] G. Ma, B.O. Patrick, T.Q. Hu, B.R. James, Acta Cryst. E 59 (2003) 0579.
- [36] S. Liu, Z.Y. Wu, N. Shan, D.D. Wang, H.J. Zhu, Acta Cryst. E 62 (2006) 01582.
- [37] E.S. Aazam, Acta Cryst. E 63 (2007) 02751.
- [38] B. Chattopadhyay, S. Basu, P. Chakraborty, S.K. Choudhury, A.K. Mukherjee, M. Mukherjee, J. Mol. Struct. 932 (2009) 90.