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DFT calculations of 2,4,6-trinitrophenylbenzoate derivatives: Structure, ground state properties and spectral properties

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ABSTRACT

2,4,6-Trinitrophenylbenzoate derivatives **3**(**a**–**g**) were synthesised and their optimum molecular geometries, ground state properties, IR, UV and NMR spectra were calculated using the B3LYP method with 6-31G** Pople basis set. The predicted geometry showed that the aryl-oxygen bond is stronger than acyloxygen bond. Bond lengths are affected by the presence of electron donating or electron withdrawing groups in benzoyl moiety. The orientation of the two aryl rings with respect to each other is neither in the same plane nor perpendicular. Hammett plot showed good linearity between substituent constant and the HOMO as well as LUMO energies. Mulliken and NBO charges indicate that the carbonyl carbon (C7) is more positively charged than the ipso carbon (C10), while the inspection of the coefficient on the carbonyl carbon and the *ipso* carbon atom for LUMO showed that its value is greater for C10 compared to C7. The correlation between the experimental and the theoretical results indicates that density functional theory B3LYP method is able to provide satisfactory results for predicting IR, UV and NMR properties.

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Recently, quantum chemical calculations have been proven to be an important tool for prediction of the relative electron den-

1. Introduction

Esters have been studied extensively due to its important role in biological, chemical, environmental industrial processes and many natural molecules [1-4]. Ester group is also used as a molecular segment in designing ferroelectric and antiferroelectric liquid crystals (FLC and AFLC) [5]. As a result, esters formation and degradation processes have been the subject of extensive experimental and theoretical studies [2–6]. It has long been known that either the acyl-oxygen bond or aryl-oxygen bond of phenyl esters can be cleaved depending on: (i) the structure of the ester [6,7] (ii) the nature of reagent [8,9] (iii) the basicity of the leaving group anion compared to that of the attacking nucleophile, (iv) the nature of substituent in the aryl or the acyl group containing the ester [8,9] and (v) the relative "hardness" and "softness" of the reaction site and reagent. Competition between the two electrophilic centers in the ester substrate is well documented for reactions of nitrophenyl sulfonates, sulfates and phosphates with nucleophiles [10-12]. On the other hand, most carboxylic esters undergo acyl-oxygen scission [10,13]. Simultaneous acyl and aryl-oxygen scission were also observed for the methanolysis of picryl benzoate under neutral conditions [7,14]. The modes of scission and the rate constants for Ar (k_{Ar}) relative to CO (k_{co}) were owing to the strong activation of the 1-position (ipso) of the phenolic group [8].

* Corresponding author. E-mail address: mohamed_elatawy@yahoo.com (M.A. El-atawy). sities on each reaction site, investigation of the relationship between structures and spectral properties of the organic molecules and for the interpretation of experimental data arising from industrial interest and applications. The density functional theory (DFT) method, which involves electron correlation effects, has proved suitable for calculating the energy-minimized structure and spectroscopic properties of phenyl benzoate derivatives [15,16]. In addition, the time-dependent density functional theory (TD-DFT) method has also been shown to be able to give good results in calculations of the electronic absorption spectra of these compounds. DFT calculations were performed in order to determine structure of 2,4,6-trinitrophenylbenzoate derivatives (3a-g), and to compare the calculated results with the experimental data. Such calculations may be used to predict the regioselectivity of these esters as precursors to study nucleophilic substitution reactions involving acyl-oxygen versus aryloxygen scissions.

2. Experimental

The UV spectra were recorded in methanol solution (C = 10^{-4} M) on a 160-A UV–VIS Shimadzu spectrophotometer. The IR spectra were recorded by FT-IR spectrometer, the ¹H NMR spectra were carried out at ambient temperature (~25 °C) on a (JEOL) 500 MHz spectrophotometer using tetramethylsilane (TMS) as an internal standard.

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2.1. Synthesis of 2,4,6-trinitrophenylbenzoate derivatives (3a-g)

A solution of picric acid (1) (1 g, 43 mmole) and the respective acid chloride (benzoyl chloride (2a), p-anisoyl chloride (2b), p-toluoyl chloride (2c), m-toluoyl chloride (2d), p-chlorobenzoyl chloride (2g), (0.62 g, 44 mmole) in (10 ml) chloroform was refluxed for 3 h [6]. Work up afforded a precipitate which was filtered and crystal-lized from chloroform-ether mixture as a crystal. The purity was checked by TLC (1:2 ethyl acetate:*n*-hexane).

2.2. 2,4,6-Trinitrophenyl benzoate (3a)

Yield: 75%; m.p: 159 °C; UV (MeOH): $\lambda_{max} = 234$ nm ($\varepsilon = 18,910$), IR (KBr): 1758 cm⁻¹ (C=O), 1545, 1341 cm⁻¹ (NO₂ asym and sym. respectively). ¹H NMR [(CD₃Cl)]: δ 9.18 (s, 2H, H_{3',5'}-picryl), 8.16 (d, *J* = 7.6, 2H, H_{2,6}-benzoyl), 7.75 (t, *J* = 7.6, 1H, H₄-benzoyl), 7.57 (t, *J* = 7.6, 2H, H_{3,5}-benzoyl). C₁₃H₇N₃O₈: requires: C, 46.86; H, 2.12; N, 12.61%. Found: C, 46.96; H, 2.07; N, 12.95%.

2.3. 2,4,6-Trinitrophenyl p-anisate (3b)

Yield: 68%; m.p: 140 °C; UV (MeOH): $\lambda_{max} = 260$ nm ($\epsilon = 23,670$), IR (KBr): 1745 cm⁻¹ (C=O), 1544, 1344 cm⁻¹ (NO₂ asym and sym. respectively). ¹H NMR [(CD₃Cl)]: δ 9.15 (s, 2H, H_{3',5'}-picryl),8.11 (d, *J* = 8.4, 2H, H_{2,6}-anisoyl), 7.02 (d, *J* = 9.1, 2H, H_{3,5}-anisoyl), 3.92 (s, 3H, OCH₃), MS (M = 363). C₁₄H₉N₃O₉: requires: C, 46.29; H, 2.50; N, 11.57%. Found: C, 45.93; H, 2.24; N, 11.32%.

2.4. 2,4,6-Trinitrophenyl p-toluate (3c)

Yield: 67%; m.p: 166 °C; UV (MeOH): $\lambda_{max} = 240 \text{ nm}$ ($\varepsilon = 22,040$), IR (KBr): 1749 cm⁻¹ (C=O), 1544, 1341 cm⁻¹ (NO₂ asym and sym. respectively). ¹H NMR [(CD₃Cl)]: δ 9.16 (s, 2H, H_{3',5'}-picryl), 8.04 (d, *J* = 8.4, 2H, H_{2,6}-toluoyl), 7.36 (d, *J* = 7.6, 2H, H_{3,5}-toluoyl), 2.48 (s, 3H, CH₃), MS (M = 347). C₁₄H₉N₃O₈: requires: C, 48.43; H, 2.61; N, 12.10%. Found: C, 48.15; H, 2.61; N, 12.39%.

2.5. 2,4,6-Trinitrophenyl m-toluate (3d)

Yield: 67%; m.p: 148 °C; UV (MeOH): $\lambda_{max} = 235$ nm ($\varepsilon = 23,950$), IR (KBr): 1752 cm⁻¹ (C=O), 1544, 1341 cm⁻¹ (NO₂ asym and sym. respectively). ¹H NMR [CD₃Cl]: δ 9.17 (s, 2H, H_{3',5'}-picryl), 7.96 (m, 2H, H_{2,4}-toluoyl), 7.55 (d, J = 7.6, 1H, H₆-toluoyl), 7.45 (t, J = 7.6, 1H, H₅-toluoyl), 2.46 (s, 3H, CH₃). C₁₄H₉N₃O₈: requires: C, 48.43; H, 2.61; N, 12.10%.Found: C, 48.63; H 2.72; N 12.23%.

2.6. 2,4,6-Trinitrophenyl p-chlorobenzoate (3e)

Yield: 78%; m.p: 166 °C; UV (MeOH): $\lambda_{max} = 240 \text{ nm}$ ($\varepsilon = 22,430$), IR (KBr): 1752 cm⁻¹ (C=O), 1538, 1338 cm⁻¹ (NO₂ asym and sym. respectively). ¹H NMR [CD₃Cl]: δ 9.18 (s, 2H, $H_{3',5'}$ -picryl), 8.09 (d, *J* = 8.4, 2H, $H_{2,6}$ -aroyl), 7.55 (d, *J* = 8.4, 2H, $H_{3,5}$ -aroyl). $C_{13}H_6CIN_3O_8$: requires: C, 42.47; H, 1.64; N, 11.43%. Found: C, 42.79; H, 1.63; N, 11.64%.

2.7. 2,4,6-Trinitrophenyl m-chlorobenzoate (3f)

Yield: 74%; m.p: 138 °C; UV (MeOH): $\lambda_{max} = 230$ nm ($\epsilon = 20,470$), IR (KBr): 1762 cm⁻¹ (C=O), 1547, 1346 cm⁻¹ (NO₂ asym and sym. respectively). ¹H NMR [CD₃Cl]: δ 9.20 (s, 2H, H_{3',5'}-picryl), 8.14 (s, 1H, H₂-Aroyl), 8.06 (dd, 1H, H₆-aroyl), 7.72 (dd, 1H, H₄-aroyl), 7.53 (t, 1H, H₅-aroyl). C₁₃H₆ClN₃O₈ requires: C, 42.47; H, 1.64; N, 11.43% .Found: C, 42.35; H, 1.45; N, 11.25%.

2.8. 2,4,6-Trinitrophenyl p-nitrobenzoate (3g)

Yield: 76%; m.p: 184 °C; UV (MeOH): $\lambda_{max} = 250$ nm ($\epsilon = 19,250$), IR (KBr): 1767 cm⁻¹ (C=O), 1548, 1349 cm⁻¹ (NO₂ asym and sym. respectively). ¹H NMR [(CD₃₎₂SO]: δ 8.55 (s, 2H, H_{3',5'}-picryl), 8.12 (d, *J* = 8.4, 2H, H_{2,6}-aroyl), 8.28 (d, *J* = 8.4, 2H, H_{3,5}-aroyl). C₁₃H₆N₄O₁₀: requires: C, 41.28; H, 1.60; N, 14.81%.Found: C, 41.28; H, 1.55; N, 15.08%.

3. Calculations

All calculations were performed using the Gaussian 98 package [17]. A conformational search for obtaining the most stable conformer was done using the semi-empirical PM3 method, the most stable conformer was subjected to full geometrical optimizations using the DFT and Becke's three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang and Parr B3LYP/6-31G** method [18-20] without any constraints to calculations. All calculated structures were found to be true minima, i.e., no imaginary frequencies were observed. After the ground state geometry optimization, the excitation spectrum of each molecule has been computed with TD-DFT [21] at the 6-31G^{**} level. ¹H NMR chemical shifts of the previously optimized 2,4,6-trinitrophenyl benzoate derivatives 3(a-g)have been calculated by using gauge-including atomic orbital GIAO/B3LYP [22–24] density functional method with 6-31G** basis set. To evaluate the relative chemical shifts, the tetramethylsilane (TMS) shielding constants calculated at B3LYP/6-31G** method.

4. Results and discussion

The reaction of equivalent amounts of picric acid and aroyl chlorides in chloroform gave 2,4,6-trinitrophenyl 4- or 3-substituted benzoates (**3a**–**g**) as indicated in Scheme 1. The purity of the compounds was confirmed from their elemental analysis and spectral measurements.

5. Molecular structure and optimized geometry

The optimized geometrical parameters (bond length, angles and dihedral angles) are listed in Table 1. The numbering of atoms for the



Scheme 1. Synthesis of 2,4,6-trinitrophenyl benzoate derivatives 3a-g.



Fig. 1. The optimized structures and atom labeling of compounds 3a-g.

optimized geometries of 2,4,6-trinitrophenylbenzoates **3**(**a**–**g**) are shown in Fig. 1. To the best of our knowledge, only the unsubstituted ester (**3a**) is previously prepared [7] and all the experimental data on geometric structure are not available in the literature.

Table. 1. Shows that the acyl-oxygen bond length (C7–O9) varies between 1.398 and 1.417 Å while the aryl-oxygen bond length (C10–O9) varies between 1.347 and 1.355 Å depending on the substituent at the acyl moiety. The shortening of the aryl-oxygen bond relative to the acyl-oxygen bond can be attributed to the large contribution of the lone pair of O9 with the trinitro groups of the picryl ring in resonance. As a result, the aryl-oxygen scission is expected to be more difficult and require higher activation energy compared to the acyl-oxygen scission when these compounds subjected to nucleophilic reactions. The C7–O8 is the carbonyl group bond length which was calculated to be (1.204 Å) for the unsubstituted ester (**3a**). In general, the presence of moderate or weak electron donating groups such as (4-CH₃, 3-CH₃) have no effect on C7–O8 bond length, whereas strong electron donating group (4-OCH₃)

shows a small increase in bond distance. While electron withdrawing groups such as 3-Cl, 4-NO₂ showed a slight decrease in bond distance. The 4-Cl substituent is expected to behave like the other electron withdrawing groups; however, it has no effect on the bond distance of carbonyl group. This is attributed to the opposite polarization effect of halogen atoms (i.e. inductive opposes resonance).

Table 1 indicates that the effect of the substituents is reversed about C1–C7 bond length. The presence of electron donating groups such as $(4-OCH_3, 4-CH_3, 3-CH_3)$ shorten the bond distance, While the presence of electron withdrawing groups $(3-Cl, 4-NO_2)$ lengthen the bond distance. As expected, the 4-chloro substituent deviates from the behavior of the other electron withdrawing groups and shorten the distance presumably due to its opposite polarization effect.

The obvious effect of the 4-OCH₃ and 4-Cl substituents in bond lengthening of C7–O8 and bond shortening of C1–C7 is due to the cross conjugation of the lone pair of this group or atom with the

Table	1
Table	

Some structure parameters of optimized geometry of 2,4,6-trinitrophenylbenzoate derivatives (3a-g) determined by B3LYP/6-31G** method.

Structural parameters	Н	4-0CH ₃	4-CH ₃	3-CH ₃	4-Cl	3-Cl	4-NO ₂
R ^a							
C7—O9	1.407	1.417	1.410	1.409	1.407	1.404	1.398
O9–C10	1.353	1.347	1.352	1.352	1.351	1.352	1.355
C7—O8	1.204	1.205	1.204	1.204	1.204	1.203	1.203
C1C7	1.473	1.462	1.469	1.472	1.472	1.476	1.480
C11-N22	1.478	1.477	1.477	1.478	1.478	1.478	1.478
C13—N19	1.475	1.473	1.474	1.475	1.474	1.475	1.476
C15—N16	1.478	1.477	1.477	1.477	1.478	1.478	1.479
A ^a							
C1-C7-09	111.46	110.79	111.42	111.52	110.79	110.77	110.80
C1-C7-08	127.54	128.18	127.72	127.62	127.54	127.43	126.98
08–C7–09	121.00	121.01	120.86	120.86	121.65	121.78	122.20
C7-09-C10	118.54	119.82	118.57	118.51	119.84	119.78	119.83
09-C10-C11	118.80	118.83	118.81	118.83	118.79	118.76	118.78
09-C10-C15	124.11	124.44	124.15	124.10	124.27	124.27	124.11
C11–C10–C15	117.01	116.73	116.95	116.98	116.94	116.96	117.11
Da							
09-C10-C11-N22	-0.40	-6.06	-0.21	-0.54	-5.04	-4.94	-0.40
09-C10-C15-N16	5.74	1.91	5.73	5.86	1.37	1.37	-0.91
08–C7–C1–C6	-2.51	4.15	-2.09	-1.49	4.87	5.20	-6.06
C7-09-C10-C11	64.50	-53.02	63.90	64.77	-54.74	-55.18	56.16
C7-09-C10-C15	-119.48	126.22	-119.64	-118.86	124.80	124.40	-123.63
C5-C6-C1-C7	179.99	180.00	179.95	179.93	179.99	-179.92	180.00
C3-C2-C1-C7	-179.92	179.84	-179.91	-180.00	179.83	179.74	-179.80
09-C10-C11-C12	177.39	177.60	177.48	177.28	178.23	178.31	-178.72
09-C10-C15-C14	-174.85	-177.90	-174.89	-174.74	-178.44	-178.48	178.87

^a **R**, bond length (Å); **A** bond angle (°); **D**, dihedral angle (°).



Fig. 2a. The resonance structures of (3b).



Fig. 2b. The molecular electrostatic calculation of compound 3b.

carbonyl group which leads to resonance structures (I–IV). These resonating structures show that the carbonyl group has some single bond character so it becomes elongated than the normal one.

Also C1—C7 bond has some double bond character, so it becomes shorter compared to the unsubstituted derivative. This effect is more pronounced in case of 4-OCH₃ substituent which has higher ability to donate it's lone pair than the electronegative chlorine atom, Fig. 2a. These resonance structures are verified from molecular electrostatic potential (MEP) [25] surface of compound **3a**, Fig. 2b.

Simply, MEP measures how attractive (blue) or repulsive (red) for any region of the molecule is to a proton placed at any point surrounding the molecule. MEP shows that the attractive region (blue) accumulates over the oxygen of the nitro groups and over the carbonyl oxygen, while the oxygen of the methoxy group and of the phenolic part of the ester appear in the red region. The bond length of the C—C bond is between 1.389–1.406 and 1.390–1.402 for aryl and trinitrophenyl rings respectively (not shown in the table) which is much shorter than the typical C—C single bond (1.54 Å) and longer than the C=C double bond (1.34 Å) [26].

Table 1 shows that the bond angles C7—O9—C10 for compounds **3a–g** are in the range of 118.50–119.83°. The calculations indicated that the O9 atom is out of plane of the picryl ring by 1.3–5.3°, and it forms only 0.20–6.06° dihedral angle with the nitrogen atom of the

nitro group, these small values are enough to suggest a negligible deviation from coplanarity with the picryl ring and explains the ability of the lone pair of O9 to involve in resonance with the nitro groups of the picryl ring. This is supported from the observed decrease in three C–N bond lengths than that normal Csp³–N single bond due to the formation of resonanting structures III.IV, Table 1. Also the C13-N19 of the 4-nitro group is shorter than those of ortho C11-N22, C15-N16 indicating a larger contribution of the 4-nitro group in resonance compared to the ortho ones. The orientation of the two phenyl rings with respect to each other can be estimated from the calculated dihedral angles between the plane of the aromatic rings and the ester group (angles around the O-Pic and CO-Ar bonds). These angles are C7-O9-C10-C11 and 08–C7–C1–C6 and are denoted by $Ø_1$ and $Ø_2$ respectively. The $Ø_2$ is very close to 0° because of the strong conjugation between the carbonyl and the aryl group. While $Ø_1$ found to be 53–64.5° depending on the substituents which indicate that the two phenyl rings are neither in the same plane nor perpendicular to each other.

6. Ground state properties

The ground state properties, namely: energies of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels and the dipole moments of compounds **3a–g** are calculated by B3LYP with 6-31G^{**} basis set, Table 2.

Inspection of Table 2 shows that the presence of electron donating groups push up the frontier molecular orbitals, while the powerful electron withdrawing nitro group pushes them down. The chloro atom in 3- or 4- position has negligible effect on rising the energy of the HOMO and lowering the LUMO energy. Attempts to illustrate the effect of substituents on the HOMO and LUMO energies were made by plotting the values of their energies against Hammett substituent constants (σ), Figs. 3 and 4. It has been seen that the σ values correlates linearly with HOMO and LUMO energies with negative slope. In other words, the substituent effect on HOMO and LUMO is straightforward: the electron donating groups (e.g. 4-OCH₃, 4-CH₃ or 3-CH₃) increase the orbital energy, while the electron withdrawing groups (e.g. 4-Cl, 3-Cl or 4-NO₂) decrease the orbital energy. It is noticed that the Hammett correlation for the LUMO energies is better than for HOMO energies, with correlation coefficients 0.99 and 0.80 respectively. Also the calculations show that the titled esters have a dipole with a negative end at the O9 and a positive end at the aroyl ring except for compound $(3g, x = 4-NO_2)$ where the positive end is oriented toward the picryl group.

Klopman equation is studied in the present work in order to investigate the relative reactivity of the two electrophilic centers namely (C7, C10) toward nucleophilic attack. The simplified form of klopman equation [27] is given below

$$\Delta E = \underbrace{\frac{-Q_{\text{nuc}}Q_{\text{elec}}}{\varepsilon R}}_{\text{electrostatic term}} + \underbrace{\frac{2(c_{\text{nuc}}c_{\text{elec}}\beta)^2}{E_{\text{HOMO}} - E_{\text{LUMO}}}}_{\text{orbital term}}$$
(1)

Table 2

The energies of frontier molecular orbitals and the dipole moments of the compounds (**3a–g**) evaluated by B3LYP/6-31G^{**} method.

	HOMO(ev)	LUMO(ev)	E(LUMO – HOMO)	μ(D)
Н	-7.5267	-3.4504	4.0763	4.1319
4-OCH ₃	-6.7827	-3.3489	3.4338	6.1581
4-CH ₃	-7.3035	-3.4019	3.9016	4.9322
3-CH ₃	-7.2031	-3.424	3.7791	4.5715
4-Cl	-7.5035	-3.5464	3.9571	2.432
3-Cl	-7.398	-3.5663	3.8317	3.4534
4-NO ₂	-8.2203	-3.7535	4.4668	1.1625



Fig. 3. Plot of LUMO energy in (eV) of compounds (3a–g) against Hammett constants (σ).



Fig. 4. Plot of HOMO energy in (eV) of compounds (3a–g) against Hammett constants (σ).

Table 3 Mulliken, NBO atomic charge and atomic orbital coefficient of LUMO for the selected centers (C7,C10).

cpd	x	Atomic orbital coefficient LUMO		NBO cl	NBO charge		Mulliken charge	
		C7	C10	C7	C10	C7	C10	
3a 3b 3c 3d 3e 3f 3g	H 4-OMe 4-Me 3-Me 4-Cl 3-Cl 4-NO ₂	0.0163 0.0189 0.0159 0.0158 0.0224 0.0230 0.0333	0.1818 0.1836 0.1804 0.1807 0.1866 0.1876 0.1741	0.831 0.818 0.829 0.831 0.824 0.827 0.826	0.370 0.377 0.371 0.370 0.372 0.371 0.367	0.623 0.604 0.621 0.624 0.612 0.616 0.620	0.406 0.401 0.407 0.406 0.396 0.394 0.391	

In this equation, Q_{nuc} and Q_{elec} are the total charges on interacting atoms of nucleophile and electrophile, ε is the local dielectric constant, R is the distance between atoms of nucleophile and electrophile, C_{nuc} is the coefficient of atomic orbital of nucleophile in HOMO, C_{elec} is the coefficient of atomic orbital of electrophile in LUMO, β is the overlap integral, E_{HOMO} is the energy of HOMO nucleophile and E_{LUMO} is the energy of LUMO electrophile. Thus the charge on atom in a molecule (q) and its electron density (C) are essential requirements for the solution of Klopman equation. In the present study the effective atomic charges calculated with usage of both Mulliken and natural bond orbital (NBO), and the atomic orbital coefficient of LUMO calculated using B3LYP method for the compounds **3a–g** are shown in Table 3. The charges and the coefficient of each compound are confined to the two centers for the nucleophilic substitution reaction, namely (C7, C10). Both



Fig. 5. Electron density diagram of LUMO's of esters 3a-g.

The Mulliken and NBO charges show that the carbonyl carbon (C7) is more positively charged than the ipso carbon (C10), and the charge does not change significantly with variation of the substituent especially within the NBO scheme.

The general inspection of the coefficient on the carbonyl carbon and the *ipso* carbon atoms in LUMO shows that its value is greater

experimental 260 TD-DFT SCRF-TD-DFT 250 240 Amax 230 220 210 200 3g 3e 3f 3b 3d 3a 3c Compound No

Fig. 7. The experimental and calculated λ_{max} values of studied 2,4,6-trinitrophenyl benzoate derivatives **3a–g**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

for C10 compared to C7 for all esters under investigation, Table 3. These values are consistent with the electron density diagram of the LUMO's of the esters **3a–g**, Fig. 5.

Thus C7 can be considered as the hard electrophilic center while C10 is the soft one. As a result, one can suggest that the regioselectivity of the nucleophilic reaction depends on the nature of the attacking nucleophile: where hard nucleophile which has low lying HOMO and usually a negatively charged, making the energy gap between LUMO of the ester and the HOMO of the nucleophile is large, so the orbital term in Klopman equation would be very small and can be neglected, in such case the reaction is referred to as charge controlled and occur selectively on the carbonyl carbon (C7) and it will be kinetically fast due to a large electrostatic attraction. While for soft nucleophile which has high lying HOMO and not necessarily have a negative charge, make the HOMO of the nucleophile and the LUMO of the ester closer to each other which led to small denominator of the orbital term, consequently the orbital term has large value and so large influence of the orbital coefficients, *c*, and the resonance integral, in this case the reaction

Table 4

Experimental UV data along with calculated λ_{max} (nm) and oscillator strength values for compounds **3a**–g.

cpd	x	Experimental	TD-DFT		SCRF-TD-DFT		Assignment of electronic transition (coeff.%)
		$\lambda_{\max} (\log \varepsilon)$	λ_{max}	f	λ_{max}	f	
3a	Н	234 (4.277)	222	0.227	225	0.324	HOMO – 1 to LUMO + 3 (30.7%)
3b	4-OCH ₃	260 (4.374)	228	0.563	232	0.676	HOMO to LUMO + 3 (36.8%)
3c	4-CH ₃	240 (4.343)	225	0.438	229	0.549	HOMO to LUMO + 3 (35%)
3d	3-CH ₃	235 (4.379)	222	0.21	225	0.28	HOMO – 1 to LUMO + 3 (26.7%)
3e	4-Cl	240 (4.351)	226	0.452	228	0.549	HOMO to LUMO + 3 (27.3%)
3f	3-Cl	230 (4.311)	222	0.227	225	0.265	HOMO – 2 to LUMO (26.5%)
3g	4-NO ₂	250 (4.284)	231	0.4	237	0.472	HOMO – 1 to LUMO + 2 (35.7%)



Fig. 6. Theoretically predicted electronic absorption spectra of compounds 3a-g.



Fig. 8. Electron density diagram for the π and π^* molecular orbitals corresponds to the electronic transitions of compounds **3a**-g.

is referred to as FMO controlled and would occur selectively on C10. However, the interactions on each center can exhibit a mixture of charge and FMO contributions for nucleophiles of intermediate lying HOMO.

7. Electronic absorption spectra

The electronic spectra of the titled compounds **3a**–**g** measured in methanol along with the theoretical electronic absorption spectra using B3LYP/6-31G^{**} level optimized structure and calculated by TD-DFT are listed in Table 4. The theoretical electronic absorptions for compounds **3a**–**g** are collected in Fig. 6. The differences between the theoretical gas-phase calculations and the experimental results are quite large. This is a reason to extend the calculation with the polarizable continuum TD-DFT (PCM-TD-DFT) [28,29] method.

In PCM the solute part lying inside a cavity, whereas the solvent part (methanol) represented as a structureless material. The solvent is also characterized by its dielectric constant and other macroscopic parameters. We have selected the non-equilibrium PCM solutions because UV/Vis spectra are studied in the present work. It has been seen from Table 4 that solvent leads to a bathochromic shift for all λ_{max} calculated. The statistical analysis of the UV data in

Table 4 shows that the mean absolute error is improved from 16 nm to 12.5 nm when the solvent effect is involved in calculation. The comparison between the experimental and the theoretical results indicates that the density functional B3LYP methods provide satisfactory results to predict UV properties, Fig. 7.

Molecular orbital analysis show that the frontier molecular orbitals are mainly composed of *p* atomic orbitals, therefore, the singlet-singlet absorptions is corresponding to π - π ^{*} type electronic transitions. To gain further insight into the nature of the electronic transition, the electron density plots of molecular orbitals mainly involved in the electronic transitions are presented in Fig. 8. It is a common feature for compounds **3a-e** that their main transitions involve the LUMO + 3 as the unoccupied orbital, so it can be considered as the π^* orbital for these compounds, however, the π^* orbital in case of compounds **3f**, **3g** is LUMO and LUMO + 2 respectively. As seen from Fig. 8. strong delocalization is present in π^* orbitals, whereas the π orbitals show more localization of the isosurfaces of the wave functions on the benzoyl moiety, except for compound 3f in which the electron density in π orbital is localized on the picryl moiety. Thus, these states correspond to an electron transfer from benzoyl moiety to the whole molecular skeleton.

Substituted 2,4,6-trinitrophenylbenzoates 3a-g show bathochromic effects when the hydrogen atom at the 3- or 4-position is replaced by a substituent, especially by introducing the strongly ouxochromic methoxy group. Weakly electron donating groups such as CH₃ and Cl have also small bathochromic effects. On the other hand, a large bathochromic shift is observed on introducing a nitro group. The effect of substituents on absorption spectra can be explained on the basis that the electron donating substituents in para-positions (4-OCH₃, 4-CH₃), the lone pair of oxygen or C–H σ -bond of methyl group elongate the conjugated system and results in a decrease of the excitation energy causing a bathochromic effect (Red shift to λ_{max}). In addition, the electron donating ability of substituents is ordered as OCH₃ > CH₃. The chloro substituent results in minor changes to λ_{max} relative to that of unsubstituted compound, which is an indicative of the induced electron attraction, as well as the joining of unshared electron pairs of chlorine in the conjugation. The bathchromic shift of the nitro group is probably due to the very polarizable character of this group.



Fig. 9. Plot of the observed versus theoretical wave number of carbonyl group of compounds 3a-g.



Fig. 10. Plot of log experimental wave number of the carbonyl group versus σ^{\dagger} .

Table 5

Calculated and experimental IR absorption (cm^{-1}) for the C=O and NO₂ bands of compounds 3a-g.

cpds	x	<i>v</i> (C=0)	v (C=0)		$\bar{\nu}_{asym}(NO_2)$		\bar{v}_{sym} (NO ₂)	
		\bar{v}_{calc}	\bar{v}_{exp}	\bar{v}_{calc}		\bar{v}_{calc}	\bar{v}_{calc}		\overline{v}_{exp}
3a	Н	1772 (251.9) ^a	1759(s)	1618	(311.9) ^a	1545(s)	1354	$(.67)^{a}$	1341.6(s)
				1613	$(230.6)^{a}$		1341	(352) ^a	
				1591	(119.9) ^a		1339	(395.6) ^a	
3b	4-0 Me	1766 (342.7) ^a	1745(s)	1615	(276) ^a	1544(s)	1354	$(3.64)^{a}$	1344(s)
				1611	(220.2) ^a		1341	(351.4) ^a	
				1587	(8.5) ^a		1338	(405) ^a	
3c	4-Me	1769 (342.7) ^a	1750(s)	1617	(296.4) ^a	1544(s)	1355	(.59) ^a	1341(s)
				1613	(230.7) ^a		1341	$(350.9)^{a}$	
				1590	(121.2) ^a		1339	(403.31) ^a	
3d	3-Me	1771 (269.3) ^a	1752(s)	1617	(323.3) ^a	1544(s)	1355	$(1.17)^{a}$	1341(s)
				1613	(230.1) ^a		1341	(349.8) ^a	
				1590	(116.6) ^a		1339	(396.9) ^a	
3e	4-CI	1770 (284.6) ^a	1752(s)	1616	(337.1) ^a	1538(s)	1353	(3.12) ^a	1338(s)
				1613	(220.6) ^a		1340	(359.6) ^a	
				1589	$(10.5)^{a}$		1338	(390) ^a	
3f	3-CI	1772 (236.8) ^a	1762(s)	1616	(356.8) ^a	1547(s)	1353	$(3.05)^{a}$	1346(s)
				1613	(221) ^a		1340	$(357.4)^{a}$	
				1589	(10.5) ^a		1338	(387.4) ^a	
	4-NO ₂	1773 (229.5) ^a	1768(s)	1616	(347.7) ^a	1548(s)	1352	(3.08) ^a	1349(s)
				1614	(227.6) ^a		1345	(198.6) ^a	
				1608	$(115.4)^{a}$		1339	$(403.6)^{a}$	
				1589	(11.3) ^a		133S	(407.1) ^a	

(s) Strong.

Proton no	X = H	4-OCH ₃	4-CH ₃	3-CH ₃	4-Cl	3-Cl	4-NO ₂
H-25	8.55 (8.16)	8.75 (8.11)	8.45 (8.04)	8.15 (7.96)	8.72 (8.09)	8.66 (8.06)	7.96 (8.12)
H-26	7.90 (7.57)	7.12 (7.02)	7.75 (7.36)	7.84 (7.45)	7.78 (7.55)	7.91 (7.53)	8.03 (8.28)
H-27	8.08 (7.75)			7.97 (7.55)		7.92 (7.72)	
H-28	7.86 (7.57)	7.26 (7.02)	7.60 (7.36)		7.72 (7.55)		8.07 (8.28)
H-29	8.48 (8.16)	8.34 (8.11)	8.35 (8.04)	8.20 (7.96)	8.42 (8.09)	8.32 (8.14)	8.18 (8.12)
H-30	9.43 (9.18)	9.45 (9.15)	9.41 (9.16)	9.41 (9.17)	9.51 (9.18)	9.54 (9.20)	9.08 (8.55)
H-31	9.53 (9.18)	9.46 (9.15)	9.50 (9.16)	9.53 (9.17)	9.48 (9.18)	9.49 (9.20)	8.78 (8.55)
H-32			2.66 (2.48)	2.01 (2.46)			
H-33		3.85 (3.92)	2.57 (2.48)	2.56 (2.46)			
H-34		4.18 (3.92)	2.06 (2.48)	2.64 (2.46)			
H-35		3.85 (3.92)					

Experimental and calculated	l chemical shift of all	protons in ppm o	f arylbenzoate	derivatives (3a-g).

Value between brackets corresponds to the experimental chemical shift.

8. The vibrational frequency

Table 6

Molecular structures of 2,4,6-trinitrophenylbenzoate derivatives 3a-g were first fully optimized at B3LYP/6-31G** level method. The observed experimental FT-IR spectra for the compounds 3a-g and theoretically predicted IR spectra obtained by DFT/ B3LYP method with 6-31G** basis set are given in Table 5. In experimental IR measurements, the most remarkable concern for these esters is directed to the C=O and NO₂ bands. The calculated vibrational frequencies are scaled by 0.961 scaling factor [30], but their values still higher than the observed ones for the majority of the normal modes. Two factors may be responsible for the discrepancies between the experimental and computed spectra: The first is the fact that the experimental value is unharmonic frequency while the calculated value is a harmonic frequency. The second reason caused by the environment [31] where the calculations have been actually done on a single molecule while the experimental values recorded in the presence of intermolecular interactions. A linearity between the experimental and calculated wave number for the carbonyl group, can be estimated by plotting the calculated versus experimental wave numbers Fig. 9. The plot shows that the strong electron donating substituent 4-OCH₃ and the 3-CH₃ substituent deviate from the fitted line. The deletion of these substituents improves the correlation significantly from 0.82 to 0.99.

The effect of substituent on the carbonyl vibrational frequency was found to be consistent with the previously discussed carbonyl bond distance, where the electron donating group increase the carbonyl group bond distance causing a decrease of its bond strength and consequently it vibrates at lower frequency or wave number. This effect is more pronounced for the strong donating 4-OCH₃ group. While the electron withdrawing groups lead to shortening and strengthening of the carbonyl group which explain its vibration at higher frequency. This observation is due to the resonance between the substituent and the carbonyl carbon which is supported from the good linear relationship between the frequency of C=O and (σ^+) of substituents Fig. 10. However, the effect of varying substituent on the vibrational frequency of the NO₂ groups is negligible, Table 5.

9. NMR spectra

Experimental and calculated chemical shift for all protons of esters **3a–g** are listed in Table 6. In comparing the experimental and theoretical result for the hydrogen chemical shifts, the correlation values are found 0.996, 0.995, 0.947, 0.995, 0.960, 0.956, 0.80 for X = H, 4-OMe, 4-Me, 3-Me, 4-Cl, 3-Cl, 4-NO₂, respectively. It can be seen that B3LYP findings are in good agreement with all the experimental results.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.09.024.

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