Scientific paper

Crystallography and DFT Studies of Synthesized Tetraketones

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Abstract

Two tetraketone derivatives, one previously reported and one novel, were synthesized, whose structures have been confirmed by elemental analyses, NMR, HPLC-MS, and IR spectroscopy. The crystal structures of synthesized tetraketones were determined using X-ray single-crystal diffraction. To analyze the molecular geometry and compare with experimentally obtained X-ray crystal data of synthesized compounds **1** (2,2'-((4-nitrophenyl)methylene)bis(5,5-dimethylcyclohexane-1,3-dione)) and **2** (2,2'-((4-hydroxy-3-methoxy-5-nitrophenyl)methylene)bis(5,5-dimethylcyclohexane-1,3-dione)), DFT calculations were performed with the standard 6-31G*(d), 6-31G**, and 6-31+G* basis sets. The calculated HOMO-LUMO energy gap for compound **1** was 4.60 eV and this value indicated that compound **1** is chemically more stable compared to compound **2** whose energy gap was 3.73 eV. Both compounds' calculated bond lengths and bond angles were in very good accordance to experimental values determined by X-ray single-crystal diffraction.

Keywords: Tetraketones; X-ray diffraction; DFT; HOMO-LUMO energies

1. Introduction

Tetraketones (2,2'-(arylmethylene)bis(5,5-dimethyl-2-cyclohexane-1,3-diones)) represent an important class of compounds that have shown beneficial pharmacological effects *in vitro*. They are widely used as important precursors in the synthesis of various acridindiones as laser dyes and some heterocyclic compounds, xanthendiones and thioxanthenes.[1] Tetraketones exhibit antioxidant, antibacterial and antiviral effects.[2] These compounds are well studied as the inhibitors of the enzyme lipooxygenase.[3] Tetraketones are being evaluated as prospective medicines in the treatment of inflammatory diseases, bronchiolitis, carcinoma, and autoimmune illnesses since lipooxygenases represent a potential target for rational drug design and identification of mechanism-based inhibitors for these conditions.[4,5]

These compounds were studied by X-ray crystallography (X-ray), nuclear magnetic resonance (NMR), and molecular modeling, revealing important information about structure and conformation, such as the presence of intramolecular hydrogen bonds.[6–9] One of the most important studies was conducted by Forsen *et al.* in 1969 when they determined by NMR that 2,2'-arylmethylene-bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-ones) are found as dienol tautomers. As a result, these compounds are referred to as tetraketones in the literature (Figure 1).[10]

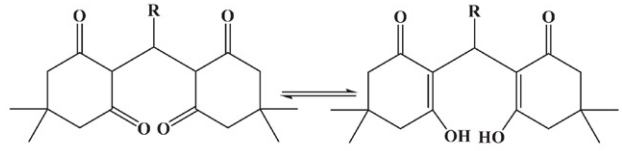

Figure 1. Tetraketones and their keto-enol tautomeric forms.

2. Materials and Methods

2. 1. Synthesis of Tetraketone (2,2'-(arylmethylene)bis(5,5-dimethyl -2-cyclohexane-1,3-dione)) Derivatives

Benzaldehyde (1 mmol), 5,5-dimethylcyclohexane-1,3-dione (2 mmol), and diazobicyclo[2.2.2]octane (DABCO) (0.05 g) were refluxed in water (20 mL). Thin-layer chromatography was used to monitor the reaction's flow and completion. Tetraketones are obtained approximately after 20 minutes of reflux. If the reflux is continued for longer (30 minutes or more), reaction leads toward formation of the 9-aryl substituted 3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-diones.[11] The mixture was cooled to room temperature, filtered, and rinsed with water once the reaction was completed. Recrystallization of the resulting compounds was performed from 96% ethanol.[12] All chemicals have been obtained from Merck (Germany).

Newly synthesized compounds were obtained through Knoevenagel condensation of aromatic aldehyde and Michael addition with 5,5-dimethylcyclohexandione-1,3-dione (Figure 2). In this article, we present two tetraketones, one previously reported (**1**)[13] and the other one novel (**2**), whose structures have been confirmed by elemental analysis, IR, NMR spectroscopy and HPLC-MS spectrometry.

2. 2. Characterization of Synthesized Products

Elemental analysis. For the synthesized tetraketone derivatives, elemental analysis was performed at the Institute of Chemistry, Technology and Metallurgy, Center for Chemistry in Belgrade, Serbia, on the Vario EL apparatus III C,H,N,S/O Elemental Analyzer, Elementar Analysensysteme GmbH, Hanau, Germany.

IR spectroscopy. IR spectra of the synthesized compounds were recorded at the Bosnalijek Pharmaceutical Company Ltd., Sarajevo, Bosnia and Herzegovina, on the Shimadzu IR Prestige 21 apparatus in the wavelength range from 4500 to 700 cm^{-1}.

NMR. ^{1}H NMR and ^{13}C NMR spectra for the synthesized compounds were recorded at the Faculty of Science in Novi Sad, Serbia, using a Bruker AC 250 E apparatus. Compounds were recorded in deuterated chloroform using TMS (tetramethylsilane) as a reference.

HPLC-MS spectra. The mass spectra were recorded on an HPLC-MS triple quadrupole 6420 autosampler (Agilent Technologies, Palo Alto, CA, USA). The recordings were made at a temperature of 573 K and a gas flow of 6 L min^{-1}. As the mobile phase, 0.1% formic acid in 50% methanol was used, at a flow rate of 0.2 mL min^{-1}. The spectra were processed using Agilent MassHunter software.

Melting point. The melting points of the synthesized compounds were determined at the Department of Pharmaceutical Chemistry, Faculty of Pharmacy in Sarajevo, Bosnia and Herzegovina, using the Melting point apparatus manufactured by Kruss Optronic, Germany.

X-ray diffraction. Single crystal measurements were performed on an Oxford Diffraction Xcalibur Nova R (microfocus Cu tube) at room temperature [293(2) K]. Program package CrysAlis PRO was used for data reduction.[14] The structures were solved using SHELXS97 and refined with SHELXL97.[15] The models were refined using the full-matrix least-squares refinement; all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were modeled as riding entities using the AFIX command.

Molecular geometry calculations were performed by PLATON,[16] and molecular graphics were prepared using ORTEP-3,[17] and CCDC-Mercury.[18] Crystallographic and refinement data for the structures reported in this paper are shown in Table 1.

Supplementary crystallographic data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/re-

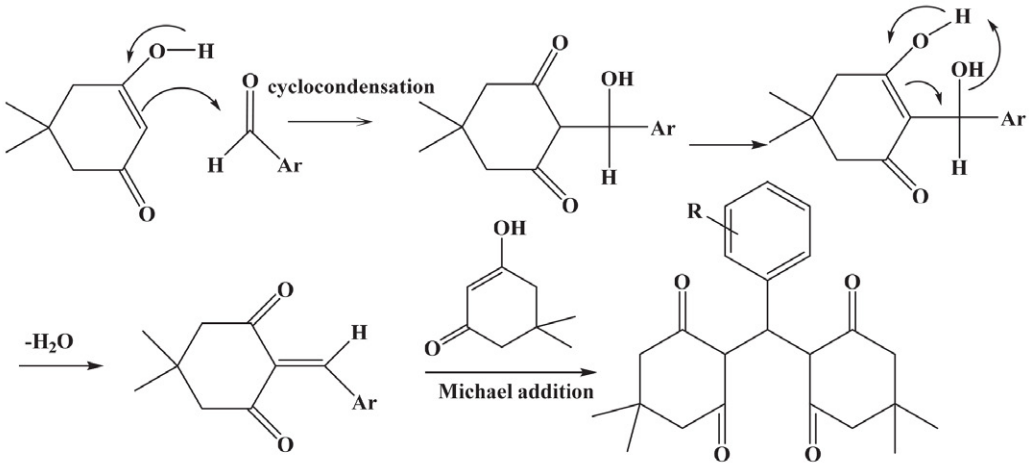

Figure 2. Synthesis of 2,2'-(arylmethylene)bis(5,5-dimethyl-2-cyclohexane-1,3-dione) derivatives.

Table 1. Crystallographic data collection and structure refinement details.

Compound	1	2
Empirical formula	$C_{23}H_{25}NO_6$	$C_{24}H_{27}NO_8$
Formula wt. / g mol^{-1}	411.45	457.47
Space group	$P\,bc2_1$	$P\bar{1}$
a / Å	23.5533(3)	8.9958(3)
b / Å	12.9754(1)	9.3891(4)
c / Å	28.1370(3)	13.9171(6)
α / °	90	98.814(4)
β / °	90	99.380(3)
γ / °	90	90.925(3)
Z	16	2
V / Å^3	8599.05(16)	1145.04(8)
D_{calc} / g cm^{-3}	1.271	1.327
μ / mm^{-1}	0.759	0.835
T / K	293(2)	293(2)
Radiation vawelength	1.54179 (Cu$K\alpha$)	1.54179 (Cu$K\alpha$)
Reflections collected	28964	10363
Independent reflections	13399	4692
Observed reflections ($I \geq 2\sigma$)	12660	4108
R_{int}	0.0212	0.0207
R (F)	0.0463	0.0488
R_w (F^2)	0.1313	0.1470
Goodness of fit	1.034	1.049
No. of parameters	1081	299
No. of restraints	1	0
Flack parameter	0.11(7)	–
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.380; –0.199	0.338; –0.168

trieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). CCDC 1990310-1990311 contains the supplementary crystallographic data for this paper.[19]

2. 3. Computational Details

Quantum chemical computations were done for compounds **1** and **2** on a single molecule in vacuo, with comprehensive geometry optimizations using standard Spartan 14 software. At the B3LYP/6-31G*, 6-31G**, and 6-31+G* levels of theory, geometry optimization was performed.[20] The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy distributions, as well as the HOMO-LUMO energy gap, were calculated using these levels of theory. The results of the DFT analysis were compared to those experimentally obtained crystallographic data.

3. Results and Discussion

3. 1. Chemistry

According to described Knoevenagel condensation of aromatic aldehyde and Michael addition with 5,5-dimethyl-1,3-cyclohexandione, we synthesized compounds **1** (2,2'-((4-nitrophenyl)methylene)bis(5,5-dimethylcyclohexane-1,3-dione)) and **2** (2,2'-((4-hydroxy-3-methoxy-5-nitrophenyl)methylene)bis(5,5-dimethylcyclohexane-1,3-dione)) (Figure 3).

The characterization of synthesized compounds **1** and **2** was achieved by FT-IR, ^{1}H and ^{13}C NMR spectroscopy, and HPLC-MS spectrometry.

1: Yield: 81%. Mp 198–203 °C. Anal. Calcd for $C_{23}H_{27}N_1O_6$: C, 66.81; H, 6.58. Found: C, 66.74; H, 6.62. IR (KBr) ν 3000 (Ar-H), 1670 (C=O), 1480 (C=C), 1300 (C-O), 1500 (C=O), 1250 (NO_2) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.8 (br s, 1H, OH, disappears with D_2O), 8.13 (d, 2H, $J_{2',3'}$ = 8.9 Hz, H-3', H-5'), 7.24 (d, 2H, $J_{2',3'}$ = 8.9 Hz, H-2', H-6'), 5.53 (s, 1H, CH), 2.21–2.57 (m, 8H, 4 × CH_2), 1.11 and 1.23 (2 × s, 12 H, 4 × CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) **δ** 190.82 (C=O), 189.46 (C-2), 146.49–146.03 (Ar-C), 127.56, 123.40 (Ar-CH), 114.81 (C-1), 46.91, 46.32 (CH_2), 33.18 (CH), 31.39 (C from $C(CH_3)_2$), 29.38, 27.38 (CH_3 from $C(CH_3)_2$). MS *m/z* (relative intensity): 412.2 (M+H).

2: Yield: 88%. Mp 230–232 °C. Anal. Calcd for $C_{24}H_{27}N_1O_8$: C, 62.73; H, 6.36. Found: C, 63.10; H, 6.08. IR (KBr) ν 3300–2500 (Ar-OH), 3042 (Ar-H), 1730 (C=O), 1607, 1588 (C=C), 1448 (O-CH_3), 1320 (C-O), 1200 (Ar-

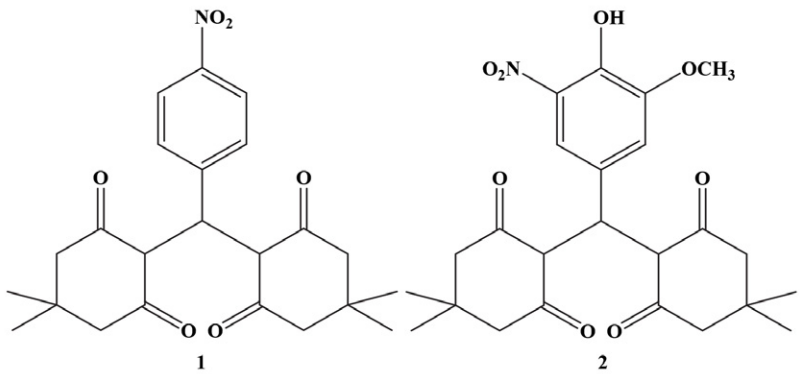

Figure 3. Structures of synthesized tetraketones **1** and **2**.

OH), 1595 (NO_2) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 10.60 (br s, 1H, OH, disappears with D_2O), 7.44 (s, 1H, H-6′), 6.90 (s, 1H, H-2′), 5.43 (s, 1H, H-13), 3.83 (s, 3H, OCH_3), 2.54–2.22 (m, 8H, H-3, H-11, H-5, H-9), 1.25 (s, 6H, H-15, H-17), 1.12 (s, 6H, H-14, H-16). ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.94 (C-6, C-8), 189.45 (C-2, C-12), 149.59 (C-3′), 144.41 (C-5′), 133.60 (C-4′), 114.71 (C-1, C-7), 117.04 (C-2′), 114.01 (C-6′), 33.18 (C-13), 31.39 (C-4, C-10), 29.82 (C-15, C-17), 26.87 (C-14, C-16). MS *m/z* (relative intensity): 460 (M+H).

3. 2. Description of the Structures

The compound **1** crystallizes in a non-centrosymmetric space group $P\,bc2_1$ with four symmetry-independent molecules in the asymmetric unit (i.e. $Z' = 4$), labeled as **a**, **b**, **c**, and **d** (Figure 4).

There are two conformers, with a different conformation of the ring C2→C6: one is comprised of molecules **a** and **d**, and the other of **b** and **c**. The rest of the molecule differs less than 3 e.s.d.'s (least-squares overlay is shown in

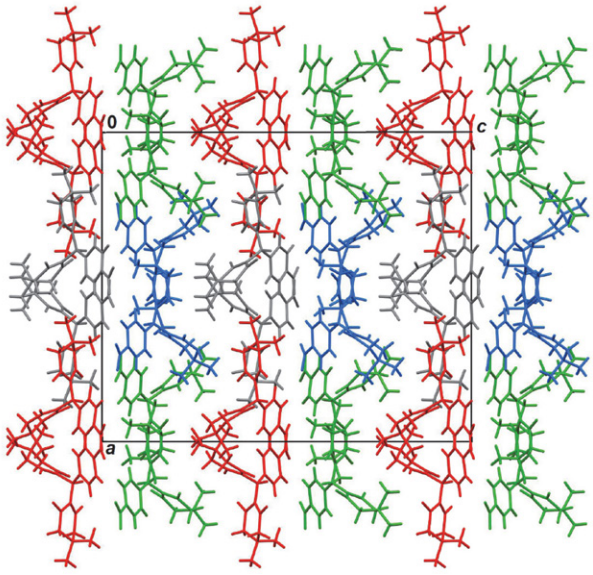

Figure 5. Crystal packing of **1** viewed in the direction [010]. Symmetry-independent molecules are shown in different colors: **a** are green, **b** are blue, **c** are red and **d** are gray.

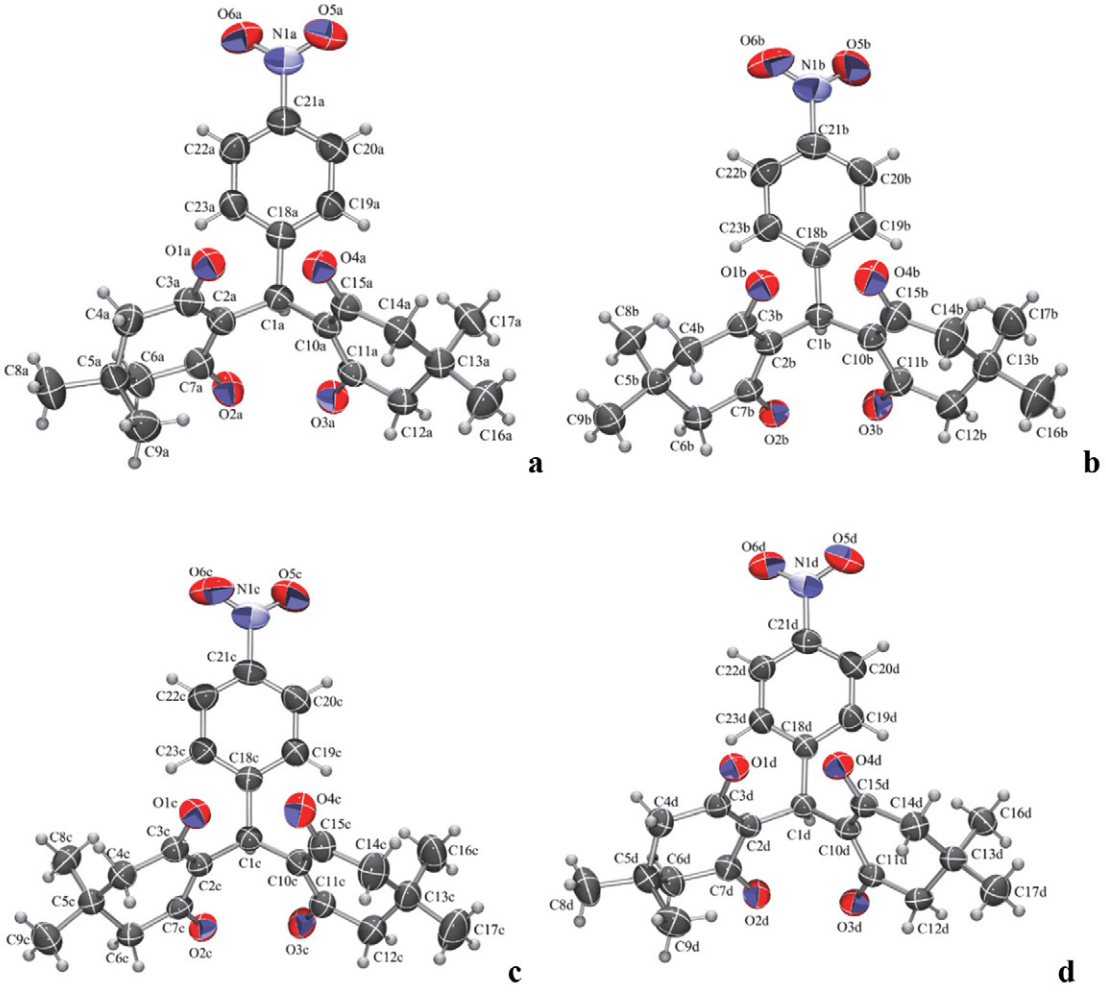

Figure 4. ORTEP-3 drawings of four symmetry-independent molecules in **1** with atom numbering schemes. Displacement ellipsoids are drawn for the probability of 50% and hydrogen atoms are shown as spheres of arbitrary radii.

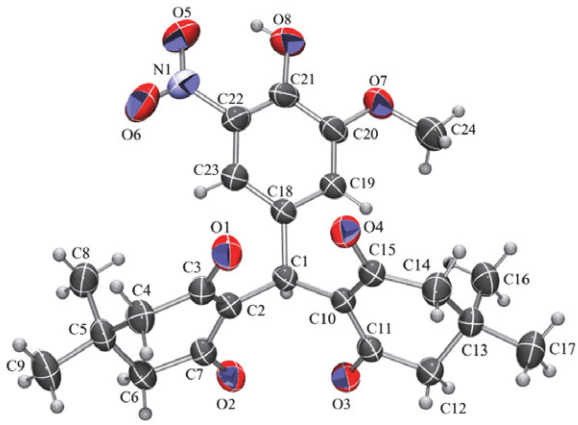

Figure 6. ORTEP-3 drawing of a molecule of **2** with the atom numbering scheme. Displacement ellipsoids are drawn for the probability of 50% and hydrogen atoms are shown as spheres of arbitrary radii.

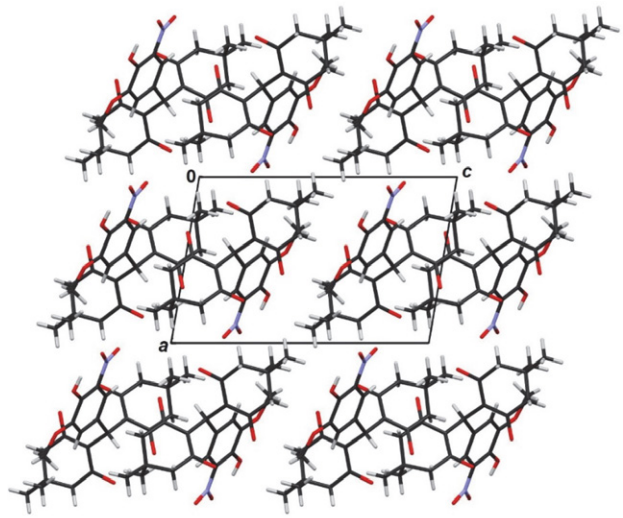

Figure 7. Crystal packing of **2** viewed in the direction [010].

Figure 8). The compound lacks proton donors and no π-stacking is observed, so 3D packing (Figure 5) is achieved mainly through dispersion interactions and weak C-H···O hydrogen bonds (Table 2).

The asymmetric unit of **2** contains one molecule (Figure 6), whose geometry and conformation are similar to those of **1** (Figure 8). The molecule possesses a single proton donor, the O8-H8 hydroxyl group, which forms an intermolecular hydrogen bond with atom O5 of the nitro group as an acceptor. Crystal data and structure refinement summary of compounds **1** and **2** are given in Tables 2 and 3. Dispersion interactions are responsible for the 3D packing (Figure 7).

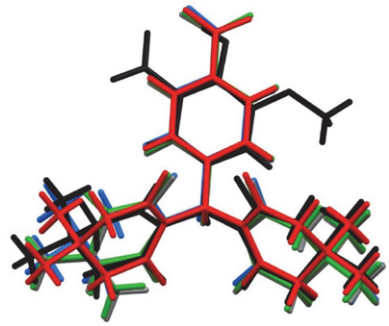

Figure 8. Least-squares overlay of four symmetry-independent molecules of **1** (**a** is green, **b** is blue, **c** is red and **d** is gray) and **2** (black).

Table 2. Geometric parameters of hydrogen bonds and angles.

Cpd (D–H···A)	d(D–H) (Å)		d(H···A) (Å)		d(D···A) (Å)		φ(D–H···A) (°)		
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Symm. op. on *A*
1									
C1A–H1A···O2A	0.98	1.01	2.41	2.38	2.855(3)	2.678	107	101	*x, y, z*
C1A–H1A···O3A	0.98	1.01	2.43	2.25	2.858(3)	2.680	106	109	*x,y, z*
C1B–H1B···O2B	0.98	1.01	2.42	2.53	2.871(3)	2.701	107	109	*x, y, z*
C1B–H1B···O3B	0.98	1.01	2.38	2.40	2.842(3)	2.710	108	110	*x, y, z*
C1C–H1C···O2C	0.98	1.01	2.41	2.47	2.863(3)	2.715	107	109	*x, y, z*
C1C–H1C···O3C	0.98	1.01	2.39	2.42	2.850(3)	2.370	108	110	*x, y, z*
C1D–H1D···O2D	0.98	1.01	2.38	2.45	2.842(3)	2.790	108	110	*x, y, z*
C1D–H1D···O3D	0.98	1.01	2.44	2.48	2.865(3)	2.800	106	109	*x, y, z*
C20B–H20B···O2A	0.93	0.99	2.54	2.60	3.295(4)	3.100	138	141	*x*, −1+*y*,*z*
C20D–H20D···O6A	0.93	0.99	2.53	2.58	3.434(4)	3.110	165	163	*x*, 3/2−*y*, 1/2+*z*
C22B–H22B···O6D	0.93	0.99	2.57	2.61	3.458(4)	3.120	160	161	1−*x*, 1−*y*, −1/2+*z*
C22D–H22D···O2D	0.93	0.99	2.51	2.56	3.199(3)	3.010	131	129	1−*x*, 1/2+*y*, *z*
2									
O8–H8···O5	0.82	0.99	1.89	1.84	2.578(3)	2.308	141	140	*x,y,z*
O8–H8···N1	0.82	0.99	2.50	2.41	2.911(2)	3.04	113	117	*x,y,z*
C1–H1···O2	0.98	1.09	2.35	2.35	2.843(18)	2.82	110	115	*x,y,z*
C1–H1···O3	0.98	1.09	2.40	2.44	2.8506(1)	2.81	108	106	*x,y,z*
C12–H12B···O1	0.97	1.09	2.53	2.84	3.480(2)	3.10	165	170	1+*x,y, z*

Table 3. Bond lengths [Å] and angles [°] of compounds **1** (molecule A, only) and **2**.

Bond length and angles	Compound 1		Compound 2	
	Exp.	Cal.	Exp.	Cal.
C1-C2	1.526(4)	1.548	1.5204(18)	1.548
C1-C10	1.528(3)	1.557	1.5246(19)	1.556
C10-C11	1.402(3	1.530	1.3944(19)	1.530
C11-C12	1.487(4)	1.520	1.499(2)	1.520
C2-C3	1.402(4)	1.546	1.395(2)	1.545
C21-O8	–	–	1.345(2)	1.340
C21-N1	1.470(4)	1.469	–	–
N1-O6	1.230(4)	1.232	1.211(3)	1.255
C7-O2	1.279(4)	1.211	1.285(19)	1.340
C11-O3	1.292(3)	1.215	1.297(19)	1.215
C2-C1-C10	113.6(2)	113.2	115.2(11)	118.0
C10-C11-O3	123.1(3)	124.0	123.0(13)	122.4
C10-C11-C12	122.2(2)	119.4	121.5(14)	121.1
C2-C3-O1	122.9(3)	120.0	123.3(13)	125.2
C2-C3-C4	122.0(2)	122.9	121.2(13)	119.9
C20-C21-C22	122.0(3)	122.7	116.9(14)	116.4
C21-N1-O5	118.4(3)	120.0	118.2(19)	119.0
C21-N1-O6	118.2(3)	119.8	119.8(16)	120.3

Compared calculated and experimentally obtained values in both Table 2 and 3 show very good accordance, differing mostly only in the second decimal place. Similar investigation and comparison of theoretical and experimental data, with good accordance for synthesized compounds, has been reported before.[21,22]

3. 3. Analysis of Molecular Orbital

The energy gap HOMO-LUMO of the molecules has a role in deciding their bioactivity and is an important parameter for quantum chemistry. The molecule becomes harder and more stable or less reactive when the HOMO-LUMO energy gap increases.[23] The HOMO energy distinguishes electron donor capacity, whereas the LUMO energy distinguishes electron acceptor capacity, and the gap defines chemical stability.[24] The energy gap HOMO-LUMO for the compounds **1** and **2** were calculated by 6-31G*, 6-31G**, and 6-31+G* basis sets and these values were –4.60, –4.57, and –4.58 for compound **1** and –3.73, –3.69, and –3.70 for compound **2**. The energies and energy gaps of HOMO and LUMO are shown in Table 4. The HOMO-LUMO orbital schemes for compounds **1** and **2** are shown in Figure 9 (the positive phases are red, and the negative phases are blue).

Compound **1** HOMO electron density demonstrates that the HOMO is localized on carbonyl carbons, methyl, and benzene, while compound **2** HOMO is concentrated on hydroxyl and methoxy groups. The HOMO-LUMO energy gap for compound **1** is 4.60 and for compound **2** is 3.73, indicating that electron density passes from carbonyl carbons, methyl, and methoxy groups to hydroxyl and nitro groups. Compound **1** has a larger HOMO-LUMO energy gap than compound **2**, making it less reactive and hence more stable. The descriptor of electron donor and acceptor is implicitly explained by the HOMO to LUMO transition to comprehend their interaction capabilities with their target molecules.

4. Conclusions

The tetraketones (compounds **1** and **2**) were successfully synthesized with excellent yield by condensation of aromatic aldehyde and Michael addition with 5,5-dimethylcyclohexane-1,3-dione. The synthesized compounds **1**

Table 4. Calculated HOMO and LUMO energy values for compounds **1** and **2**.

Parameters	Compound 1			Compound 2		
	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-31+G*	B3LYP/6-31G*	B3LYP/6-31G**	B3LYP/6-31+G*
E_{HOMO} (eV)	–6.85	–6.87	–6.84	–6.85	–6.87	–6.84
E_{LUMO} (eV)	–2.25	–2.30	–2.26	–2.53	–2.58	–2.54
Energy gap (Δ)	4.60	4.57	4.58	3.73	3.69	3.70

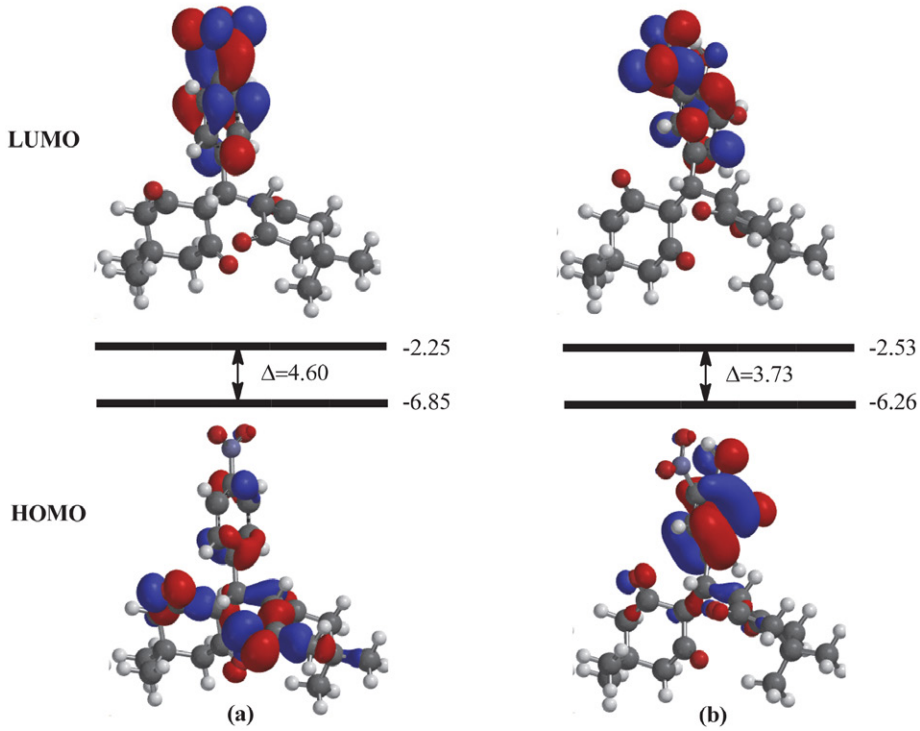

Figure 9. Frontier molecular orbitals of compound **1** (**a**) and compound **2** (**b**). All values are in eV.

and **2** were characterized using ^{1}H and ^{13}C NMR, FTIR, HPLC-MS methods, and elemental analysis. Using single-crystal X-ray diffraction data, we presented the structural details of tetraketone compounds **1** ($C_{23}H_{25}NO_6$) and **2** ($C_{24}H_{27}NO_8$). To analyze the molecular geometry and compare it to experimentally available X-ray crystal data of investigated compounds, DFT calculations were done using a standard 6-31G*(d), 6-31G**, and 6-31+G* basis sets. For compound **2**, the computed HOMO-LUMO energy gaps for basis sets 6-31G*(d), 6-31G**, and 6-31+G* were 3.73, 3.69, and 3.70, respectively. Compound **2** is chemically more reactive than compound **1** based on these smaller gap values. The theoretically determined HOMO-LUMO energy gaps can be employed to describe the biological activity of the title compounds. The crystal structure is stabilized by both intramolecular and intermolecular hydrogen bonds, with the intermolecular N–H···O hydrogen bond in compound **2** generating the N1 and O8 chain motif. The bond lengths and angles calculated for compounds **1** and **2** were in very good accordance with the experimental values obtained from X-ray crystal diffraction.

5. References

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Povzetek

Sintetizirali smo dva tetraketonska derivata (enega novega in enega že znanega) ter njuni strukturi potrdili z elementno analizo, NMR, HPLC-MS in IR spektroskopijo. Kristalne strukture sintetiziranih tetraketonov smo določili z rentgensko difrakcijsko analizo monokristalov. S pomočjo DFT računskih metod s standardnimi baznimi seti 6-31G*(d), 6-31G** in 6-31+G* smo izvedli analizo molekulske geometrije in dobljene rezultate primerjali z eksperimentalnimi, ki so bili pridobljeni z rentgensko difrakcijo pripravljenih spojin **1** (2,2'-((4-nitrofenil)metilen)bis(5,5-dimetilcikloheksan-1,3-dion)) in **2** (2,2'-((4-hidroksi-3-metoksi-5-nitrofenil)metilen)bis(5,5-dimetilcikloheksan-1,3-dion)). Izračunana vrednost HOMO-LUMO energijske špranje za spojino **1** je 4.60 eV, kar kaže, da je spojina **1** kemijsko bolj stabilna kot spojina **2**, katere velikost energijske špranje je 3.73 eV. Izračunane dolžine vezi in koti se za obe spojini zelo dobro ujemajo z eksperimentalnimi vrednostmi, dobljenimi z rentgensko difrakcijo monokristala.