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Structural characterization of new 2-aryl-5-phenyl-1,3,4-oxadiazin-6-ones and their *N*-aroylhydrazone precursors

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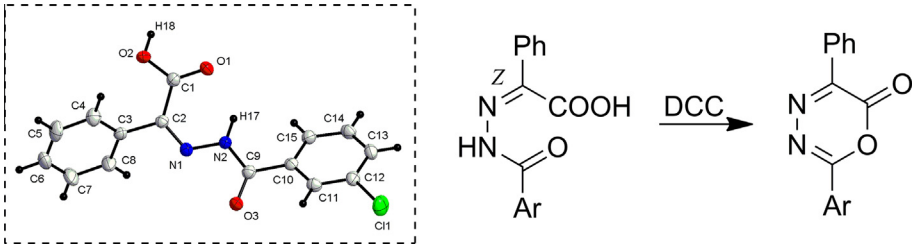
HIGHLIGHTS

- New oxadiazinones by intramolecular cyclization of corresponding *N*-aroylhydrazones.
- Electronic properties of oxadiazinones are mainly influenced by the 2-aryl substituent.
- Isolation of *Z*,*anti* isomer of *N*-aroylhydrazones.
- Strong intermolecular interactions in the solid state revealed for *N*-aroylhydrazones.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of novel 2,5-disubstituted 1,3,4-oxadiazin-6-ones and their *N*-aroylhydrazone precursors were synthesized and characterized by NMR and UV–Vis spectroscopy. The electronic properties of 2-aryl-5-phenyl-1,3,4-oxadiazin-6-ones are mainly dependent on the 2-aryl substituent and their absorption maxima exhibit a red shift in dichloromethane. Single crystal X-ray diffraction on four acylhydrazones indicated the isolation of isomer with *Z* configuration of the C=N double bond. Intermolecular interactions through strong H-bonding and C—H···π contacts serve to link the molecules into a three-dimensional supramolecular network.

1. Introduction

1,3,4-Oxadiazin-6-ones are known as valuable substrates for access to a wide variety of bicyclic and heterocyclic compounds by their [2 + 2] and [4 + 2] cycloaddition reactions with alkynes, alkenes and cycloalkenes [1–20]. The oxadiazinones act as electron deficient 2,3-diaza-1,3-butadienes playing the role of diene in Diels–Alder reactions with reversed electron demand, when γ-ketoketene are formed after loss of nitrogen from the initially produced cycloadduct [6,7,19]. Recently, their reactivity in cycloaddition reaction has found a new application in obtaining organic semiconductors such as polycyclic aromatic hydrocarbons, which are known for their electrical properties. Thus, the Diels–Alder reactions of some 2,5-diaryl-6-oxo-1,3,4-oxadiazine-6-one with benzyne or naphthyne in order to obtain linear polyacenes were reported [21,22]. When cycloaddition is performed under acidic catalysis (trifluoroacetic acid), enol-lactone derivatives are obtained without γ-ketoketene intermediate formation [7]. An exception was reported for 2,5-diphenyl-1,3,4-oxadiazin-6-one, playing the role of dienophile component when reacted with 2,3-dimethyl-1,3-butadiene [9].

The synthesis of the first member of this class of heterocycles, 2,5-diphenyl-1,3,4-oxadiazin-6-one, was reported by Steglich [10], and the first oxadiazinones bearing an alkyl side chain in position 2 or 5 was obtained by Padwa [7]. Later, a considerable number of derivatives with aryl and alkyl substituents were reported by Christl [2,3,6,9,11,12,18,19]. These works describe oxadiazinones

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as versatile substrates in cycloaddition reactions, revealing interesting application in the synthesis of various compounds, such as cyclopenta[*c*]pyrans [17]. An efficient four-step synthetic pathway leading to oxadiazinones was recently developed starting from α-aminoacid esters by a sequence of diazotation, reduction and acylation reactions, followed by cyclization of the resulted *N*-acylhydrazones [23]. A series of 1,3,4-oxadiazinylacetates were obtained in rather low yields as side products along with oxadiazepine derivatives by the condensation reaction of several carbohydrazides with dimethyl but-2-ynediolate [24].

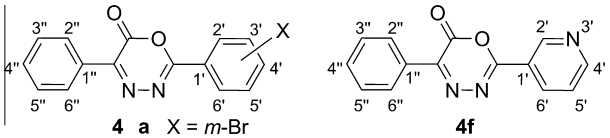
The acylhydrazones are of particular interest due to the various applications, such as electrophilic reagents in many reactions, as well as their biological activity [25–28]. Moreover, acylhydrazones are known for their ability to bind transitional metals forming complexes with antibacterial activity [29–31].

In this context, we focused in this work on the synthesis and investigation of the absorption properties of some new 2,5-diaryl-oxadiazinone derivatives and their corresponding precursors, *N*-acylhydrazones. Single crystal X-ray diffraction on four *N*-acylhydrazones revealed the isolation of the *Z,anti* isomer, stabilized by intramolecular N—H···O hydrogen bonds.

2. Experimental

2.1. General remarks

Chemicals and solvents of commercial grade were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 at room temperature on Brucker Avance 300 and Brucker Avance 500 spectrometers (δ in ppm, J in Hz); spectra were referenced using the solvent signal as internal standard. The numbering of the compounds used for assigning the NMR spectra signals was done arbitrary (for acylhydrazones **3** the same numbering as in the ORTEP diagrams was used, for oxadiazinones **4** see Chart 1). The EI mass spectra were recorded on a GC–MS Shimadzu QP 2010 spectrometer. HRMS in APCI mode ionization were recorded with an LTQ XL ThermoScientific mass spectrometer. UV–Vis absorption spectra were measured on a Cecil 9500 spectrophotometer using quart cuvettes (1 cm); the solutions for acylhydrazones **3** were 3.0 $\times 10^{-5}$ M and all solutions for oxadiazinones **4** were 4.0 $\times 10^{-5}$ M. Melting points were measured with a Kleinfeld melting point apparatus and are uncorrected. The single crystals were obtained from DMSO:methanol = 1:1 by gel method using agar-agar gel [32]. Data were collected at room temperature on a Bruker SMART APEX diffractometer, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). For this purpose the crystal was mounted on a cryo-loop with Paratone-N oil. The structure was solved by direct methods (SHELXS-97) [33] and refined by full matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97) [33]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were introduced in their idealized positions, except for the hydrogen atom of the carboxyl group which was identified from the electron density map, and refined as riding. Further details on the data collection and refinement methods can be found in Table 1. The drawings were created with the Diamond program [34].



4 **a** X = *m*-Br
b X = *m*-Cl
c X = *m*-OMe
d X = *p*-*t*Bu
e X = *p*-HO

4f

Chart 1. Numbering of oxadiazinones **4a–f.**

2.2. Synthesis of hydrazones **3**

2.2.1. General procedure

A solution of **1** (5.2 mmol) in water (60 mL) was added dropwise (over 1–2 h) under vigorous stirring to a solution of hydrazide **2** (5.2 mmol) in water (60 mL) heated to 50–60 °C. The mixture was stirred for additional 2 h, and then cooled on an ice bath until the complete precipitation of the white solid. After filtration, the solid was successively washed with cold water and cold diethyl ether (or 2-propanol). The hydrazones have been used in the next step without further purification.

2.2.2. 2-(2-(3-Bromobenzoyl)hydrazono)-2-phenylacetic acid (**3a**)

Yield 93%, white solid, m.p. 177–178 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 7.39–7.49 (overlapped peaks, 3H, H_5, H_6, H_7), 7.53 (t from overlapped dd, 1H, J = 7.8 Hz, H_{14}), 7.62–7.76 (m, 2H, H_4, H_8), 7.84 (overlapped peaks, 2H, H_{13}, H_{15}), 8.02 (d, 1H, J = 0.6 Hz, H_{11}), 12.70 (s, 1H, N*H*). ^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 121.4, 128.1, 128.3, 128.7, 129.6, 131.0, 134.5, 135.2, 135.5, 164.0, 165.4. UV/Vis (1,4-dioxane) λ_{max} (log ε) = 236 (4.16), 315 (4.21) nm. EI–MS m/z (rel. int.) = 44 (31), 50 (46), 51 (32), 65 (10), 76 (53), 89 (18), 103 (34), 119 (6), 139 (12), 155 (34), 157 (31), 183 (100), 185 (99), 199 (39), 201 (37), 301 (9), 303 (9), 345 (2), 347 (0.2) [M$^+$]. MS (APCI+): 347.0 [M+H]$^+$, 303.0 [M–CO_2]$^+$. HRMS (APCI+): calcd for $C_{15}H_{12}BrN_2O_3$ [M+H]$^+$: 347.0026; found: 347.0023.

2.2.3. 2-(2-(3-Chlorobenzoyl)hydrazono)-2-phenylacetic acid (**3b**)

Yield 96%, white solid, m.p. 178–179 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 7.41–7.48 (overlapped peaks, 3H, H_5, H_6, H_7), 7.60 (t from overlapped dd, 1H, J = 7.8 Hz, H_{14}), 7.66–7.73 (overlapped peaks, 3H, H_4, H_8, H_{13}), 7.80 (d, 1H, J = 7.8 Hz, H_{15}), 7.86–7.88 (br. s, 1H, H_{11}), 12.75 (s, 1H, N*H*). ^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 127.4, 128.2, 128.3, 128.8, 129.7, 130.8, 132.1, 134.5, 135.1, 135.3, 164.0, 165.4. UV/Vis (1,4-dioxane) λ_{max} (log ε) = 236 (4.14), 316 (4.23) nm. EI–MS m/z (rel. int.) = 39 (3), 44 (10), 50 (12), 51 (10), 65 (6), 75 (23), 76 (23), 89 (4), 103 (60), 111 (45), 113 (15), 139 (100), 141 (34), 155 (53), 157 (18), 257 (10), 302 (0.2) [M$^+$]. MS (APCI+): 303.1 [M+H]$^+$, 259.1 [M–CO_2]$^+$. HRMS (APCI+): calcd for $C_{15}H_{12}ClN_2O_3$ [M+H]$^+$: 303.0531; found: 303.0525.

2.2.4. 2-(2-(3-Methoxybenzoyl)hydrazono)-2-phenylacetic acid (**3c**)

Yield 94%, white solid, m.p. 173–174 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 3.83 (s, 3H, OCH_3), 7.22 (d, 1H, J = 8.1 Hz, H_{13}), 7.40–7.52 (overlapped peaks, 6H, H_5, H_6, H_7, H_{11}, H_{14}, H_{15}), 7.64–7.74 (m, 2H, H_4, H_8), 12.87 (s, 1H, N*H*). ^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 55.4, 112.8, 118.2, 119.5, 128.2, 128.4, 129.4, 130.2, 134.3, 134.9, 159.5, 164.1, 165.4. UV/Vis (1,4-dioxane) λ_{max} (log ε) = 235 (4.19), 315 (4.21) nm. EI–MS m/z (rel. int.) = 39 (4), 44 (8), 63 (12), 64 (14), 76 (13), 77 (25), 92 (21), 103 (50), 107 (45), 121 (7), 135 (100), 151 (74), 253 (11), 298 (0.3) [M$^+$]. MS (APCI+): 299.1 [M+H]$^+$, 255.1 [M–CO_2]$^+$. HRMS (APCI+): calcd for $C_{16}H_{15}N_2O_4$ [M+H]$^+$: 299.1026; found: 299.1022.

2.2.5. 2-(2-(4-tert-Butylbenzoyl)hydrazono)-2-phenylacetic acid (**3d**)

Yield 92%, white solid, m.p. 175–176 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 1.32 (s, 9H, C(CH_3)$_3$), 7.40–7.47 (overlapped peaks, 3H, H_5, H_6, H_7), 7.59 (d, 2H, J = 8.4 Hz, H_{12}, H_{14}), 7.65–7.72 (m, 2H, H_4, H_8), 7.80 (d, 2H, J = 8.4 Hz, H_{11}, H_{15}), 13.02 (s, 1H, N*H*). ^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 30.9, 34.8, 125.8, 127.4, 128.1, 128.4, 129.3, 130.1, 135.0, 155.4, 164.1. UV/Vis

Table 1
Summary of crystal data and structure refinements for compounds **3a**, **3b**, **3k**, **3l**.

Compound	**3a**	**3b**	**3k**	**3l**
Empirical formula	$C_{15}H_{11}BrN_2O_3$	$C_{15}H_{11}ClN_2O_3$	$C_{16}H_{14}N_2O_3$	$C_{15}H_{12}N_2O_3$
Formula weight	347.17	302.71	282.29	268.27
Crystal size (mm)	0.60 × 0.45 × 0.21	0.46 × 0.18 × 0.17	0.41 × 0.23 × 0.23	0.60 × 0.33 × 0.29
Crystal habit	Yellow block	Colorless block	Colorless block	Colorless block
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Temperature (K)	297(2)	297(2)	297(2)	297(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	Pbca	Pbca	P2(1)/c	Pbca
a (Å)	16.052(3)	16.160(4)	7.8312(18)	12.308(3)
b (Å)	10.3456(18)	10.317(3)	22.132(5)	13.392(3)
c (Å)	17.054(3)	16.666(4)	8.750(2)	16.241(4)
α (°)	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	111.392(4)	90.00
γ (°)	90.00	90.00	90.00	90.00
Volume (Å^3)	2832.2(8)	2778.6(12)	1412.2(6)	2677.1(10)
Z	8	8	4	8
Density (calculated) (g cm^{-1})	1.628	1.447	1.328	1.331
Absorption coefficient (mm^{-1})	2.914	0.286	0.093	0.095
F (000)	1392	1248	592	1120
θ range for data collections (°)	2.39–25.00	2.44–25.00	1.84–25.00	2.51–25.00
T_{max}/T_{min}	0.5797/0.2738	0.9530/0.8796	0.9789/0.9627	0.9731/0.9454
Reflections collected	19,085	18,795	13,411	23,881
Independent reflections, R_{int}	2495, 0.0570	2448, 0.0656	2495, 0.0430	2350, 0.0513
Completeness to θ = 25.00°	100%	100%	100%	99.9%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2495/0/195	2448/0/194	2495/0/199	2350/0/186
Goodness-of-fit on F^2	1.055	1.202	1.230	1.335
Final *R* indicies [$I > 2\sigma(I)$]	R_1 = 0.0408	R_1 = 0.0683	R_1 = 0.0813	R_1 = 0.0799
	wR_2 = 0.0956	wR_2 = 0.1214	wR_2 = 0.1599	wR_2 = 0.1456
R indices (all data)	R_1 = 0.0552	R_1 = 0.0821	R_1 = 0.1010	R_1 = 0.0887
	wR_2 = 0.1005	wR_2 = 0.1270	wR_2 = 0.1691	wR_2 = 0.1497
Largest diff. peak and hole, e A^{-3}	0.470, −0.310	0.226, −0.227	0.210, −0.237	0.176, −0.173
CCDC No.	921311	921308	921309	921310

(1,4-dioxane) λ_{max} ($\log\varepsilon$) = 235 (4.23), 316 (4.34) nm. EI–MS *m*/*z* (rel. int.) = 44 (26), 50 (18), 51 (24), 65 (6), 76 (22), 91 (53), 103 (44), 118 (24), 134 (17), 146 (20), 161 (100), 162 (92), 177 (31), 279 (7), 325 (0.3) [M$^+$]. MS (APCI+): 325.2 [M+H]$^+$, 281.2 [M–CO_2]$^+$. HRMS (APCI+): calcd for $C_{19}H_{21}N_2O_3$ [M+H]$^+$: 325.1547; found: 325.1544.

*2.2.6. 2-(2-(4-Hydroxybenzoyl)hydrazono)-2-phenylacetic acid (**3e**)*

Yield 95%, white solid, m.p. 203–204 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm: 6.92 (d, 2H, *J* = 8.8 Hz, H_{12}, H_{14}), 7.43–7.45 (overlapped peaks, 3H, H_5, H_6, H_7), 7.66–7.68 (m, 2H, H_4, H_8), 7.75 (d, 2H, *J* = 8.8 Hz, H_{11}, H_{15}), 10.32 (s, 1H, N*H*). ^{13}C NMR (125 MHz, DMSO-d_6) δ ppm: 115.6, 123.1, 128.1, 128.4, 128.9, 129.2, 130.2, 135.2, 161.4, 164.2, 165.4. UV/Vis (1,4-dioxane) λ_{max} ($\log\varepsilon$) = 235 (4.20), 296 (4.35) nm. EI–MS *m*/*z* (rel. int.) = 39 (13), 44 (8), 65 (40), 76 (9), 93 (48), 103 (42), 121 (100), 137 (63), 239 (13), 284 (0.2) [M$^+$]. MS (APCI+): 285.1 [M+H]$^+$, 241.1 [M–CO_2]$^+$. HRMS (APCI+): calcd for $C_{15}H_{13}N_2O_4$ [M+H]$^+$: 285.0870; found: 285.0867.

*2.2.7. 2-(2-Nicotinoylhydrazono)-2-phenylacetic acid (**3f**)*

Yield 91%, white solid, m.p. 199–120 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 7.35–7.53 (overlapped peaks, 3H, H_5, H_6, H_7), 7.55–7.80 (overlapped peaks, 3H, H_4, H_8, H_{14}), 8.23 (d, 1H, *J* = 7.8 Hz, H_{15}), 8.80 (d, 1H, *J* = 3.3 Hz, H_{13}), 9.01 (br. s, 1H, H_{11}), 12.82 (s, 1H, N*H*). ^{13}C NMR (75 MHz, DMSO-d_6) δ ppm: 123.9, 128.3, 128.8, 129.7, 130.4, 134.5, 135.3, 148.4, 151.9, 164.1, 165.4. UV/Vis (1,4-dioxane) λ_{max} ($\log\varepsilon$) = 235 (4.12), 311 (4.27) nm. EI–MS *m*/*z* (rel. int.) = 44 (32), 50 (41), 51 (98), 52 (29) 65 (7), 76 (28), 78 (100), 89 (12), 103 (58), 106 (98), 122 (70), 148 (9), 224 (25), 270 (0.2) [M$^+$]. MS (APCI+): 270.1 [M+H]$^+$, 226.1 [M–CO_2]$^+$. HRMS (APCI+): calcd for $C_{14}H_{12}N_3O_3$ [M+H]$^+$: 270.0873; found: 270.0873.

*2.3. Synthesis of 1,3,4-oxadiazin-6-ones (**4**)*

*2.3.1. General procedure (for compounds **4a**–**d**, **4f**)*

A solution of dicyclohexylcarbodiimide (DCC) (3.48 mmol) in absolute THF (5 mL) was added, under argon, to a stirred solution of *N*-aroylhydrazone carboxylic acid **3** (3.48 mmol) in absolute THF (30 mL), and the mixture was stirred at *rt* for 24 h. The white solid, consisting of *N*,*N*′-dicyclohexylurea, was filtered off and the solvent was removed under vacuum. The obtained yellow solid was triturated with dry diethyl ether to give pure **4**.

*2.3.2. 2-(3-Bromophenyl)-5-phenyl-6H-1,3,4-oxadiazin-6-one (**4a**)*

Yield 87%, yellow solid, m.p. 154–155 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.44 (t from overlapped dd, 1H, *J* = 8.0 Hz, $H_{5'}$), 7.48–7.63 (overlapped peaks, 3H, $H_{3''}$, $H_{4''}$, $H_{5''}$), 7.76 (ddd, 1H, *J* = 8.0, 1.9, 1.0 Hz, $H_{4'}$), 8.22 (dt, 1H, *J* = 8.0, 1.0 Hz, $H_{6'}$), 8.31–8.35 (m, 2H, *J* = 7.4 Hz, $H_{2''}$, $H_{6''}$), 8.44 (t from overlapped dd, 1H, *J* = 1.9 Hz, $H_{2'}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 123.2, 126.6, 128.6, 129.1, 129.4, 130.5, 130.7, 130.9, 132.2, 136.5, 147.7, 153.1, 156.2. UV/Vis (acetonitrile) λ_{max} ($\log\varepsilon$) = 248 (sh, 3.84), 333 (4.30) nm; (1,4-dioxane) λ_{max} ($\log\varepsilon$) = 238 (3.88), 336 (4.28) nm; (ethyl acetate) λ_{max} ($\log\varepsilon$) = 335 (4.29) nm; (dichloromethane) λ_{max} ($\log\varepsilon$) = 227 (3.98), 250 (3.80), 343 (4.29) nm. EI–MS *m*/*z* (rel. int.%) = 50 (12), 63 (30), 76 (28), 89 (29), 155 (41), 157 (39), 183 (100), 185 (95), 328 (5), 330 (5) [M$^+$]. MS (APCI+): 329.0 [M+H]$^+$, 301.0 [M–N_2]$^+$. HRMS (APCI+): calcd for $C_{15}H_{10}BrN_2O_2$ [M+H]$^+$: 328.9920; found: 328.9922.

*2.3.3. 2-(3-Chlorophenyl)-5-phenyl-6H-1,3,4-oxadiazin-6-one (**4b**)*

Yield 99%, yellow solid, m.p. 137–138 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.47–7.63 (overlapped peaks, 5H, $H_{5'}$, $H_{4'}$, $H_{3''}$, $H_{4''}$, $H_{5''}$), 8.18 (dt, 1H, *J* = 7.8, 1.4 Hz, $H_{6'}$), 8.24 (t from overlapped dd,

1H, J = 1.8 Hz, $H_{2'}$), 8.32–8.35 (m, 2H, $H_{2''}$, $H_{6''}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 126.4, 128.2, 128.8, 129.3, 129.4, 130.5, 130.9, 132.4, 133.8, 135.5, 147.9, 153.3, 156.5. UV/Vis (acetonitrile) λ_{max} ($\log\varepsilon$) = 243 (3.89), 332 (4.32) nm; (1,4-dioxane) λ_{max} ($\log\varepsilon$) = 242 (3.86), 334 (4.33) nm; (ethyl acetate) λ_{max} ($\log\varepsilon$) = 333 (4.33) nm; (dichloromethane) λ_{max} ($\log\varepsilon$) = 225 (3.86), 249 (3.86), 342 (4.33) nm. EI–MS m/z (rel. int.) = 41 (6), 55 (10), 57 (13), 63 (18), 75 (19), 89 (17), 111 (47), 113 (16), 139 (100), 141 (33), 284 (5) $[M]^+$. MS (APCI+): 285.0 $[M+H]^+$; 257.0 $[M-N_2]^+$. HRMS (APCI+): calcd for $C_{15}H_{10}ClN_2O_2$ $[M+H]^+$: 285.0425; found: 285.0428.

*2.3.4. 2-(3-Methoxyphenyl)-5-phenyl-6H-1,3,4-oxadiazin-6-one (**4c**)*

Yield 92%, yellow solid, m.p. 99–100 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 3.91 (s, 3H, OCH_3), 7.18 (ddd, 1H, J = 8.1, 2.3, 1.1 Hz, $H_{4'}$), 7.46 (t from overlapped dd, 1H, J = 8.1 Hz, $H_{5'}$), 7.48–7.61 (overlapped peaks, 3H, $H_{3''}$, $H_{4''}$, $H_{5''}$), 7.81 (t from overlapped dd, 1H, J = 2.3 Hz, $H_{2'}$), 7.87 (dt, 1H, J = 8.1, 1.1 Hz, $H_{6'}$), 8.32–8.36 (m, 2H, $H_{2''}$, $H_{6''}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 55.6, 112.1, 120.6, 120.7, 128.6, 128.7, 129.0, 130.1, 131.0, 132.1, 148.1, 152.7, 157.4, 159.9. UV/Vis (acetonitrile) λ_{max} ($\log\varepsilon$) = 220 (sh, 4.22), 252 (sh, 3.85), 338 (4.33) nm; (1,4-dioxane) λ_{max} ($\log\varepsilon$) = 254 (3.80), 340 (4.28) nm; (ethyl acetate) λ_{max} ($\log\varepsilon$) = 339 (4.25) nm; (dichloromethane) λ_{max} ($\log\varepsilon$) = 228 (4.05), 256 (3.81), 347 (4.29) nm. EI–MS m/z (rel. int.) = 63 (16), 77 (21), 92 (16), 107 (17), 135 (100), 280 (5) $[M^+]$. MS (APCI+): 281.1 $[M+H]^+$, 253.1 $[M-N_2]^+$. HRMS (APCI+): calcd for $C_{16}H_{13}N_2O_3$ $[M+H]^+$: 281.0921; found: 281.0922.

*2.3.5. 2-(4-tert-Butylphenyl)-5-phenyl-6H-1,3,4-oxadiazin-6-one (**4d**)*

Yield 85%, yellow solid, m.p. 114–115 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.38 (s, 9H, $C(CH_3)_3$), 7.48–7.58 (overlapped peaks, 5H, $H_{3'}$, $H_{5'}$, $H_{3''}$, $H_{4''}$, $H_{5''}$), 8.22 (d, 2H, J = 8.8 Hz, $H_{2'}$, $H_{6'}$), 8.31–8.35 (m, 2H, $H_{2''}$, $H_{6''}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 31.2, 35.1, 124.7, 126.3, 128.3, 128.8, 129.1, 131.3, 132.1, 148.5, 152.6, 158.0. UV/Vis (acetonitrile) λ_{max} ($\log\varepsilon$) = 249 (3.98), 340 (4.37) nm; (1,4-dioxane) λ_{max} ($\log\varepsilon$) = 249 (3.93), 340 (4.33) nm; (ethyl acetate) λ_{max} ($\log\varepsilon$) = 253 (3.82), 340 (4.25) nm; (dichloromethane) λ_{max} ($\log\varepsilon$) = 254 (3.96), 348 (4.33) nm. EI–MS m/z (rel. int.%) = 41 (3), 56 (10), 77 (5), 91 (7), 118 (12), 146 (12), 161 (100), 306 (3) $[M^+]$. MS (APCI+): 307.1 $[M+H]^+$, 279.1 $[M-N_2]^+$. HRMS (APCI+): calcd for $C_{19}H_{19}N_2O_2$ $[M+H]^+$: 307.1441; found: 307.1440.

*2.3.6. 5-Phenyl-2-(pyridin-3-yl)-6H-1,3,4-oxadiazin-6-one (**4f**)*

Yield 88%, yellow solid, m.p. 138–139 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.49–7.62 (overlapped peaks, 4H, $H_{5'}$, $H_{3''}$, $H_{4''}$, $H_{5''}$), 8.31–8.35 (m, 2H, $H_{2''}$, $H_{6''}$), 8.53 (dt, 1H, J = 8.1, 2.1 Hz, $H_{6'}$), 8.86 (dd, 1H, J = 4.9, 2.1 Hz, $H_{4'}$), 9.49 (dd, 1H, J = 2.1, 0.8 Hz, $H_{2'}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 123.7, 123.8, 128.6, 129.0, 130.5, 132.3, 134.2, 135.2, 147.4, 149.2, 153.4, 153.7. UV/Vis (acetonitrile) λ_{max} ($\log\varepsilon$) = 238 (sh, 3.96), 330 (4.35) nm; (1,4-dioxane) λ_{max} ($\log\varepsilon$) = 238 (3.78), 333 (4.18) nm; (ethyl acetate) λ_{max} ($\log\varepsilon$) = 332 (4.38) nm; (dichloromethane) λ_{max} ($\log\varepsilon$) = 242 (3.83), 339 (4.30) nm. EI–MS m/z (rel. int.) = 65 (8), 76 (32), 78 (88), 89 (22), 103 (66), 106 (100), 251 (0.3) $[M^+]$. MS (APCI+): 252.1 $[M+H]^+$, 224.1 $[M-N_2]^+$. HRMS (APCI+): calcd for $C_{14}H_{10}N_3O_2$ $[M+H]^+$: 252.0768; found: 252.0769.

*2.3.7. Procedure for **4e***

Acetic anhydride (53.02 mmol) was added to a suspension of **3e** (3.52 mmol) in absolute THF (30 mL), and the mixture was stirred for 4 h at 50 °C. The solvent and excess of acetic anhydride were removed under vacuum. Anhydrous diethyl ether was added to the oily residue and a light yellow solid precipitated. The solid was washed with cold anhydrous diethyl ether (4 × 30 mL) and dried under vacuum (3–4 h).

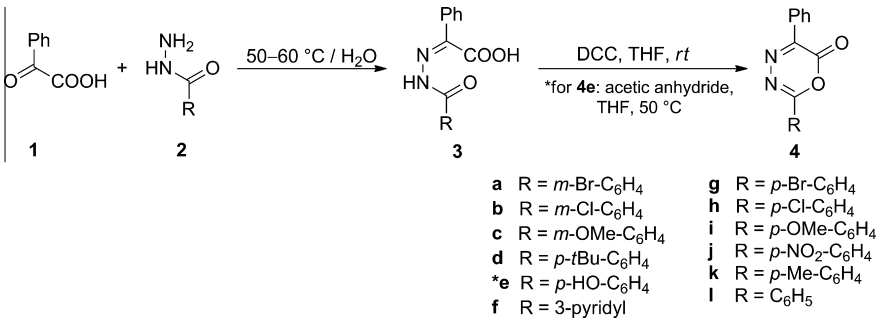
*2.3.8. 2-(4-Hydroxyphenyl)-5-phenyl-6H-1,3,4-oxadiazin-6-one (**4e**)*

Yield 80%, pale-yellow solid, m.p. 202–206 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.45 (d, 2H, J = 9.0 Hz, $H_{3'}$, $H_{5'}$), 7.49–7.62 (overlapped peaks, 3H, $H_{3''}$, $H_{4''}$, $H_{5''}$), 8.31–8.35 (m, 2H, $H_{2''}$, $H_{6''}$), 8.41 (d, 2H, J = 9.0 Hz, $H_{2'}$, $H_{6'}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 121.5, 126.8, 128.7, 129.1, 130.1, 130.8, 132.3, 147.7, 153.0, 153.1, 156.3. UV/Vis (acetonitrile) λ_{max} ($\log\varepsilon$) = 256 (3.96), 352 (4.29) nm; (1,4-dioxane) λ_{max} ($\log\varepsilon$) = 254 (3.91), 353 (4.25) nm; (ethyl acetate) λ_{max} ($\log\varepsilon$) = 341 (4.40) nm; (dichloromethane) λ_{max} ($\log\varepsilon$) = 256 (3.89), 358 (4.24) nm. EI–MS m/z (rel. int.) = 39 (11), 57 (21), 63 (11), 77 (13), 93 (40), 103 (39), 104 (30), 105 (12), 121 (100), 137 (11), 239 (48), 266 (6) $[M^+]$. MS (APCI+): 267.1 $[M+H]^+$, 239.1 $[M-N_2]^+$. HRMS (APCI+): calcd for $C_{15}H_{11}N_2O_3$ $[M+H]^+$: 267.0764; found: 267.0769.

3. Results and discussion

A series of new 2,5-diaryl-1,3,4-oxadiazin-6-ones **4a–f** (Scheme 1, Table 2) was synthesized in very good yields by using the literature procedure [10,35]. The two-steps method started with the obtaining of aroylhydrazones **3a–f** by the condensation reaction of phenylglyoxylic acid (**1**) with various commercially available aroylhydrazines **2a–f** (Scheme 1, Table 2). Next, the intramolecular esterification of **3a–f,** in the presence of DCC (except for compound **4e**, where acetic anhydride was used instead of DCC), led to the target 4,5-diaza-α-pyrones **4**. After purification by several crystallizations from diethyl ether in order to remove the residual byproduct *N*,*N*′-dicyclohexylurea, the compounds **4a–f** were fully characterized.

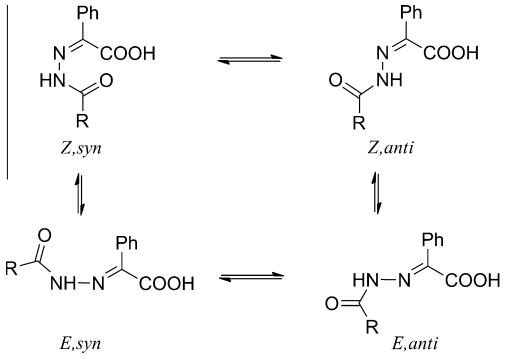
In order to study the photophysical properties of acylhydrazones **3** and oxadiazinones **4**, as well as the influence of the 2-aryl substituent, some previously reported *p*-substituted 2-aryl derivatives were also synthesized. As for derivatives **3g–l** and **4g–l**, these were obtained according to the literature [2,3,9,36].



Scheme 1. Two-steps synthesis of 2,5-diaryl-1,3,4-oxadiazin-6-ones **4a–f** *via N*-aroylhydrazones **3a–f**.

Table 2
Yields of *N*-aroylhydrazones **3a–f** and 2,5-diaryl-oxadiazinones **4a–f.**

R group	Compnd.	Yield (%)	Compnd.	Yield (%)
m-Br-C_6H_4	**3a**	93	**4a**	87
m-Cl-C_6H_4	**3b**	96	**4b**	99
m-OMe-C_6H_4	**3c**	94	**4c**	92
p-*t*Bu-C_6H_4	**3d**	92	**4d**	85
p-HO-C_6H_4	**3e**	95	**4e**	80
3-Pyridyl	**3f**	91	**4f**	88



Scheme 2. Possible isomers of hydrazones **3.**

Acylhydrazones of type **3** may exhibit geometric isomerism with respect to the C═N bond (Scheme 2), while *Z* and *E* isomers can also appear as *syn* and *anti* isomers due to a hindered rotation around the N—N single bond. The *Z* isomer was obtained as the major product, while the corresponding *E* diastereoisomer, although observable in some cases was present in the reaction mixture in less than 10%. This is in agreement with literature data, the isomer exhibiting the bulkiest groups in *trans* disposition being predominant, while the *anti* conformation is favored when polar solvents, such as DMSO, are used [37–40].

Compounds **3a–f** showed quite low solubility in most common organic solvents, still they are fairly soluble in dimethylsulfoxide or dimethylformamide and slightly soluble in 1,4-dioxane. The ^{1}H NMR spectra of **3a–f**, recorded in DMSO-d_6, display the characteristic signals for the aromatic protons along with a singlet in the range 10.32–13.02 ppm corresponding to the NH proton (see Fig. S1 in SI). The APCI and EI mass spectra of acylhydrazones **3a–f** exhibit the molecular peak $[M]^+$ albeit of low abundance (<1%) due to rapid loss of CO_2, and the peak corresponding to the $[M–CO_2]^+$ fragment (7–25%). The higher abundance peaks present in the EI mass spectra were assigned to further cleavage fragments such as $[PhCO]^+$, $[PhCN]^+$, $[RCO]^+$ or $[RCN]^+$.

The investigations of the molecular structure of hydrazones **3a**, **3b**, **3k** and **3l** (Fig. 1) by single-crystal X-ray diffraction revealed the isolation in the solid state of the isomer with *Z,anti* configuration, which seems to be the preferred spatial arrangement for these compounds [41–44]. The asymmetric unit of compound **3b** consists of a single molecule, in which a strong intramolecular N—H···O hydrogen bond ensures the *anti* disposition [O(1)···H(17) = 1.95 Å, Σr_{cov}(O,H) = 1.40 Å and Σr_{vdW}(O,H) = 2.60 Å, and the angle O1---H17—N2 = 132.68°] [45]. In case of the other three aroylhydrazones **3a**, **3k** and **3l**, the intramolecular N—H···O hydrogen bonds are about the same length, except for **3a** measuring 2.01 Å.

In the lattice, the supramolecular arrangement of the molecules is ensured by a number of non-covalent interactions (Fig. 2, Table 3). Intermolecular interactions through strong H-bonding [*e.g.* for **3b**: O(3)---H(18) = 1.88 Å, Σr_{cov}(H,O) = 0.96 Å, Σr_{vdW}(H,O) = 2.60 Å, O(3)---H(18)—O(2) = 154.2(2)°] result in a ribbon-like supramolecular association, which are further associated through edge-to-face H···π contacts [*e.g.* for **3b**: H14---centroid (C3—C8) = 2.80(1) Å, lateral shift 0.25 Å and H6---centroid (C10—C15) = 2.92(1) Å, lateral shift 0.28 Å, Σr_{vdW}(C,H) = 3.05 Å] (Table 3), except for **3k** revealing a face-to-face H···π interaction (Fig. 2, Table 3). In addition, in case of halogenated derivatives **3a** and **3b**, notable halogen bonding interactions X---O═C (Fig. 2, Table 3) contribute to the three-dimensional network. It is worthy to mention the shorter X---O distance determined for **3a** [Br(1)---O(1) = 3.15(1) Å, Table 3] as compared to **3b** [Cl(1)---O(1) = 3.25(1) Å, Σr_{vdW}(O,Cl) = 3.30 Å] [45,46]. The additional halogen bond interaction is probably responsible for the orthogonal disposition of the benzene units in compounds **3a** and **3b**, which displays an dihedral angle of 90.0(1)° and 88.7(1)° (Table 3),

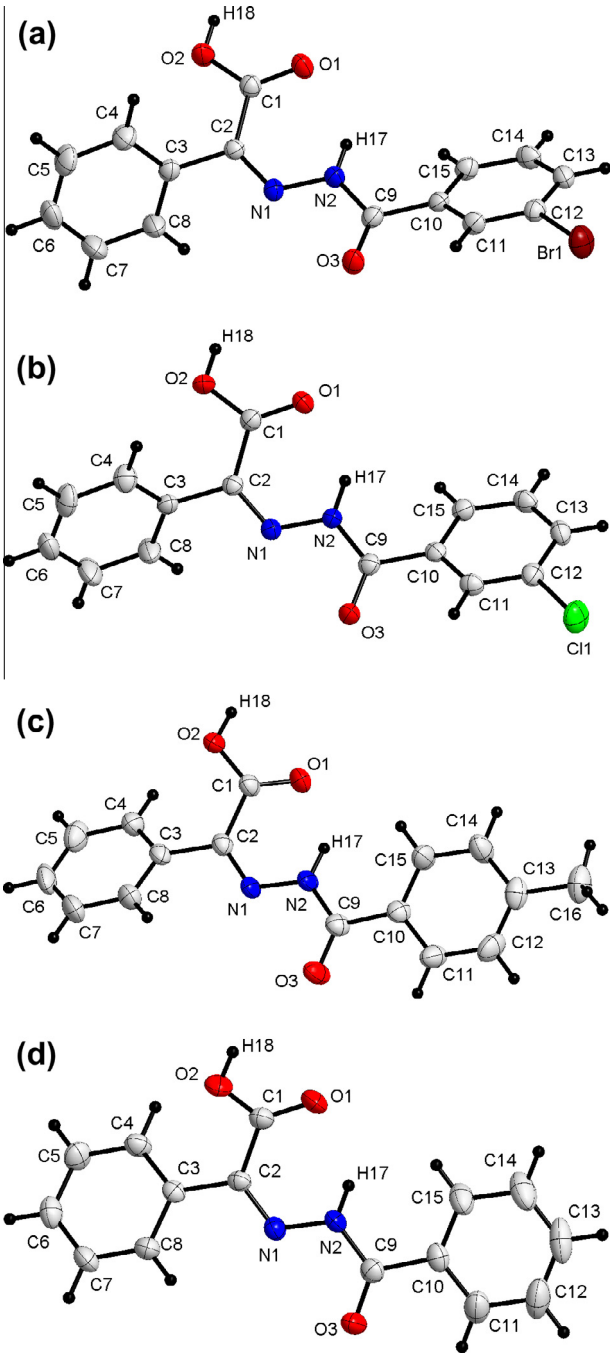


Fig. 1. View of the asymmetric unit of *N*-aroylhydrazones **3a** (a), **3b** (b), **3k** (c) and **3l** (d) with 40% probability ellipsoids.

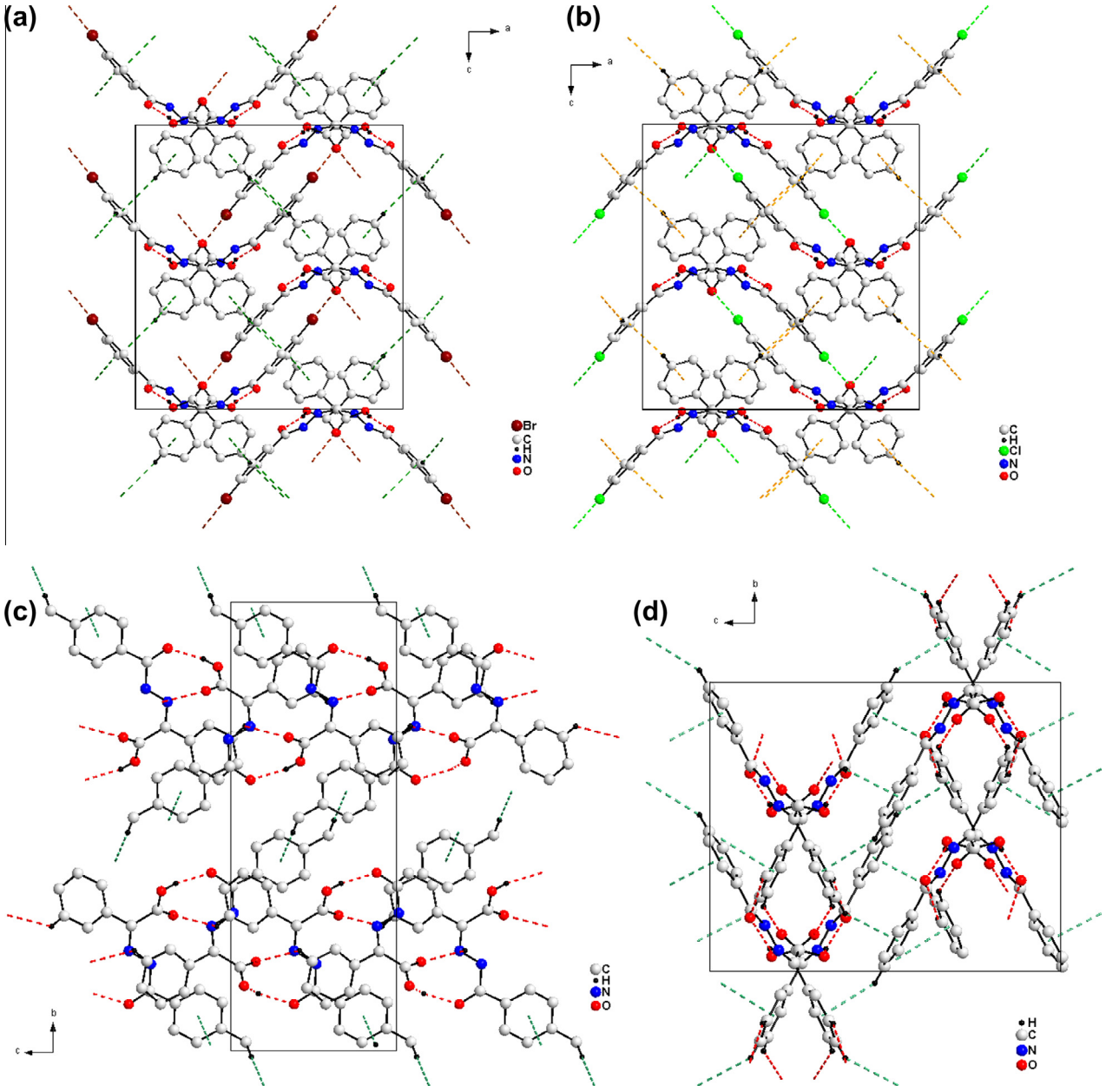


Fig. 2. Crystal packing view of *N*-aroylhydrazones (only hydrogen atoms involved in interactions are shown): unit cell view along *b* axis, showing the supramolecular associations through H-bonding, H···π contacts and C—O···X interactions in crystalline **3a** (a) and **3b** (b), respectively; unit cell view along *a* axis, showing the supramolecular associations through hydrogen bonds and H···π contacts for **3k** (c) and **3l** (d), respectively.

respectively, while in **3k** and **3l** the benzene rings lies almost coplanar, in a bisectional orientation (dihedral angle of 33.1(1)° and 19.5(1)°, Table 3).

The structure of oxadiazinones **4a–f** has been determined by ^{1}H and ^{13}C NMR spectra based on one- and two-dimensional NMR experiments. The protons of the 5-phenyl group exhibit the same pattern for all oxadiazinone derivatives, displaying three overlapped signals for H-3″, H-4″ and H-5″ in the range 7.50–7.60 ppm, and more deshielded overlapped signals corresponding to H-2″ and H-6″ (Chart 1). Considering the 2-aryl substituents, four distinct signals were assigned accordingly to *meta*- or *para*-substituted benzene, respectively (see Table S1 in SI).

The UV–Vis spectra of acylhydrazones **3** (Fig. 3a) recorded in 1,4-dioxane (dissolved after ultrasonation for 30 min. at 50 °C, then cooled to room temperature) consist of two different bands and exhibit the longest absorption maxima in the optical range 311–319 nm for **3a–l**, except for **3e** presenting λ_{max} at 296 nm. The intramolecular cyclization of hydrazones **3** to the corresponding oxadiazinones **4** causes a red shift of the longest wavelength absorption band of about 18–56 nm for the later (Fig. 3). The electronic spectra of oxadiazinones **4** shows absorption maxima in the optical range 236–254 nm and intense broad absorption bands in the area 333–356 nm, which are typical for $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions (Fig. 3b).

The analysis of the absorption properties showed basically no significant influence of the R substituent in the acylhydrazone series **3**. On the other hand, the comparison of UV–Vis spectra of parent oxadiazinone **4l** (334 nm) with **4a–k** revealed a bathochromic shift, especially for the *para*-substituted-2-aryl derivatives **4e** and **4g–j** (Fig. 3b). The most notable influence of the substituent was noticed in case of **4e** (351 nm) and **4i** (356 nm), bearing the *p*-hydroxy and *p*-methoxy-phenylene group, respectively. This

Table 3
Selected intermolecular interactions through H-bonding, H···π contacts and halogen bonds for **3a**, **3b**, **3k** and **3l** (bonds in Å, angles in °).

	3a	**3b**	**3k**	**3l**
O3---H18	1.88	1.88	1.83	1.92
O3---H18—O2	154.1(2)	154.2(2)	162.1(1)	139.5(1)
H---O	–	–	H7---O1: 2.62(1)	H7---O3: 2.68(2)
C—H---O	–	–	C7—H7---O1: 133.7(1)	C7—H7---O3: 146.9(1)
H5---O1	–	–	–	2.52(2)
C5—H5---O1	–	–	–	146.5(1)
H14---centroid (C3—C8)	2.85(1)	2.80(1)	–	–
H14 (lateral shift)	0.29	0.25	–	–
H6---centroid (C10—C15)	2.97(1)	2.92(1)	–	2.85(1)
H6 (lateral shift)	0.32	0.28	–	0.26
H16c---centroid (C10—C15)	–	–	2.87(1)	–
H16c (lateral shift)	–	–	0.53	–
H13---centroid (C3—C8)	–	–	–	2.96(1)
H13 (lateral shift)	–	–	–	0.38
H---π	Edge-to-face	Edge-to-face	Face-to-face	Edge-to-face
X1---O1	3.15(1)	3.25(2)	–	–
X1---O1—C1	167.0(2)	165.4(1)	–	–
Dihedral angle between benzene rings	90.0(1)	88.7(1)	33.1(1)	19.5(1)

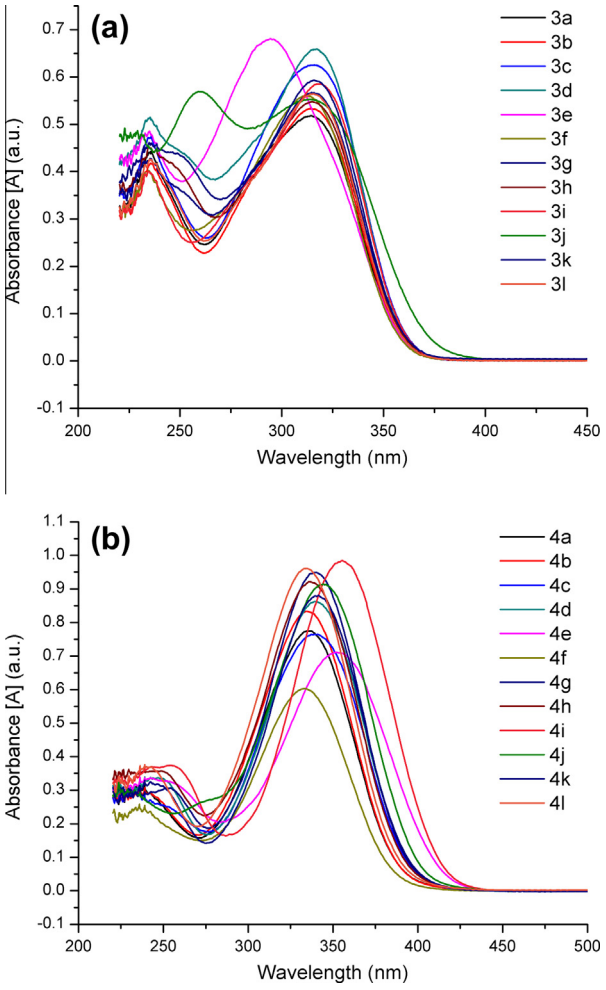


Fig. 3. Absorption spectra of *N*-aroylhydrazones **3a**–**l** in 1,4-dioxane (3×10^{-5} M) (a) and of oxadiazinones **4a**–**l** (b) in 1,4-dioxane (4×10^{-5} M).

behavior could be explained by the enhancement of electron delocalization in conjugation system, which is also observable to a less extent for the *p*-nitro derivative **4j** (344 nm). The influence of the electron delocalization effect is more obvious when compared the absorption maxima and molecular extinction coefficient of **4i** (356 nm, $\log\varepsilon = 4.40$) bearing the *p*-methoxy-phenylene group with *m*-methoxy derivative **4c** (339 nm, $\log\varepsilon = 4.29$), where only the –I effect occurs.

The impact of the substituent on the electronic spectra determined in 1,4-dioxane generally shows the same trend when recorded in dichloromethane, ethyl acetate and acetonitrile (see Fig. S2 in SI). However, a red shift could be observed for the *p*-nitro derivative **4j** (354 nm) and a blue shift for the *p*-hydroxy derivative **4e** (340 nm), when ethyl acetate was used. Besides, oxadiazinone **4i**, showed a constant bathochromic (15–20 nm) along with hyperchromic effect in all solvents. The influence of the solvent has been observed as generally causing a larger bathochromic shift in dichloromethane in contrast to the hypsocromic shift in more polar acetonitrile.

4. Conclusions

In summary, we report herein the good yield synthesis of some new 2-aryl-5-phenyl-1,3,4-oxadiazin-6-ones through DCC-assisted intramolecular cyclization of the corresponding *N*-aroylhydrazones. The analysis of absorption spectra of oxadiazinones **4** and their acylhydrazones **3** precursors, has revealed a bathochromic effect at the conversion of **3** to the corresponding 4,5-diaza-α-pyrones **4**. To the best of our knowledge, this is the first report on the electronic properties of oxadiazinone derivatives. It was noticed that the absorption spectra were mainly dependent on the 2-aryl substituent of oxadiazinones **4**. By comparing the results obtained for compounds **4** in dichloromethane, ethyl acetate, 1,4-dioxane and acetonitrile, the longest wavelength absorption maxima generally exhibit a red shift in dichloromethane. The solid state molecular structure investigations of *N*-aroylhydrazones **3a**, **3b**, **3k** and **3l** revealed the isolation of *Z,anti* isomer, stabilized by strong intramolecular H-bonding. As inferred in the lattice, the molecules pack in a ribbon-like formation as a result of strong intermolecular H-bonding, C—H···π contacts and also halogen bonds in case of **3a** and **3b**, leading to a three-dimensional supramolecular network.

Acknowledgements

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Appendix A. Supplementary material

The supplementary crystallographic data for this paper have been deposited at the Cambridge Crystallographic Data Center, deposition numbers CCDC 921311 (**3a**), CCDC 921308 (**3b**), CCDC 921309 (**3k**) and CCDC 921310 (**3l**). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.11.005.

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