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# Crystal Structure Study on Non-Coplanarly Organized Accumulating Aromatic Rings Molecules: Spatial Organization of *C*,*C*,*N*-Triaryl Substituted Imines

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## ABSTRACT

The X-ray crystal structures of *C*,*C*,*N*-triaryl-substituted imine compounds, which have methoxy or hydroxy group adjacent to the imino moiety, are reported and discussed in comparison with those of the precursor ketone compounds, 1-(4-chlorobenzoyl)-2,7-dimethoxynaphthalene and 1-(4-chlorobenzoyl)-2-hydroxy-7-methoxynaphthalene. In crystals, three aromatic rings in a molecule of the methyl ether-retained imine compound are positioned almost perpendicularly to each other by giving non-coplanar spatial organization of the single molecular structure [dihedral angles: 85.32(18)˚ for *C*-linked phenyl ring and naphthalene ring; 79.27(17)˚ for *N*-linked phenyl ring and naphthalene ring; 84.78(17)˚ for *C*-linked phenyl ring and *N*-linked phenyl ring]. Spatial organization of the analogous methyl ether-cleaved imine compound has essentially same topology [dihedral angles 80.39(6)˚ for the *C*-linked phenyl ring and naphthalene ring; 82.35(6)˚ for the *N*-linked phenyl ring and naphthalene ring; 87.09(7)˚ for *C*- and *N*-linked phenyl rings]. These structural features of triarylimines apparently differ from those of the precursor ketones. Two aromatic rings in the methyl ether-cleaved ketone compound make smaller dihedral angle [58.10(6)˚] by intramolecular hydrogen bond between ketonic carbonyl group and hydroxy group [2.5573(16) Å] than that of the methyl ether-retained ketone [72.06(7)˚]. In molecular packing, the methyl ether-retained imine forms tubular molecular alignments composed of *R*—*S* dimeric molecular pairs, whereas the methyl ether-retained ketone affords consecutively stacks of one configurated molecules.

**Keywords:** Non-Coplanarly Accumulated Aromatic Rings; Spatial Organization; Triarylimine

## 1. Introduction

Non-coplanarly accumulated aromatic-rings compounds, e.g., biphenyls and binaphthyls, have been demonstrated as unique building blocks in construction for many functional materials such as molecular catalysis and functional polymers [1-12]. Thus, minute spatial structural characterization of these compounds [13-16] has attracted attention of the chemists in the wide-range of organic molecular science and polymer materials fields. However, intra- and inter-molecular interactions that afford various functions to such molecular units still remain ambiguous. As one of the protocols to estimate such interactions, the authors have been investigating synthesis and X-ray crystal structure analysis of congested spatial organization of aromatic rings accumulating molecules.

Recently, the authors have reported specific and characteristic electrophilic aromatic aroylation of naphthalene derivatives, *i.e.*, *two* aroyl groups are regioselectively and effectively introduced at the 1,8-positions of the naphthalene ring accompanying with simultaneously proceeding retroaroylation behavior [17,18]. The 1-aroylated naphthalenes, which correspond to the intermediates in the diaroylation, are also obtained by choice of acidic mediator.

X-ray crystal structure study has revealed that the aroyl groups in these *peri*-aroylated naphthalene molecules are non-coplanarly attached to the naphthalene rings by giving crowded molecular organization [19-22]. In a natural consequence, the authors have planned to introduce additional aromatic ring planes to the core part of the aroylnaphthalene molecules for realization of more crowded inner spatial situation in accumulated aro- matic-rings molecule. As one of the molecular transfor- mation approaches to obtain such spatial organization, the authors designed conversion of ketonic carbonyl group

on 1-aroylnaphthalene to imino moiety by the re- action with aniline derivative. Imination of 1-aroylated 2,7-dimethoxynaphthalene with aromatic amines scarcely proceeded with conventional additives except for $TiCl_4$ and 1,4-diazabicyclo[2.2.2]octane (DABCO) mixture. In $TiCl_4$—DABCO mediated imination, triaryl-substituted imine compounds were formed in moderate conversion with/without preceding methyl ether cleavage reaction of the starting compound (**Scheme 1**) [23]. The neighboring ketonic carbonyl group of *peri*-aroylated 2,7-dimethoxynaphthalene derivatives plausibly accelerates $TiCl_4$-mediated scission of rather stable ether bonding.

In this article, the authors report and discuss the single molecular spatial organizations and the molecular packing characteristics of *C*,*C*,*N*-triarylated imine compounds by comparing with those of original ketone compounds: 1-aroyl-2,7-dimethoxynaphthalene and 1-aroyl-2-hydroxy-7-methoxynaphthalene.

## 2. Experimental

All reagents were of commercial quality and were used as received. Solvents were dried and purified using standard techniques.

### 2.1. Measurements

$^1$H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (300 MHz) and a JEOL ECX400 spectrometer (400 MHz). Chemical shifts are expressed in ppm relative to internal standard of $Me_4Si$ ($\delta$ 0.00). $^{13}$C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (75 MHz). Chemical shifts are expressed in ppm relative to internal standard of $CDCl_3$ ($\delta$ 77.0). IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. Elemental analyses were performed on a Yanaco CHN CORDER MT-5 analyzer. High-resolution FAB mass spectra were recorded on a JEOL MStation (MS700) ion trap mass spectrometer in positive ion mode.

### 2.2. Synthetic Procedure

Starting material **1** and triarylimines were prepared as follows.

#### 2.2.1. Electrophilic Aromatic Substitution Aroylation of 2,7-Dimethoxynaphthalene by $AlCl_3$

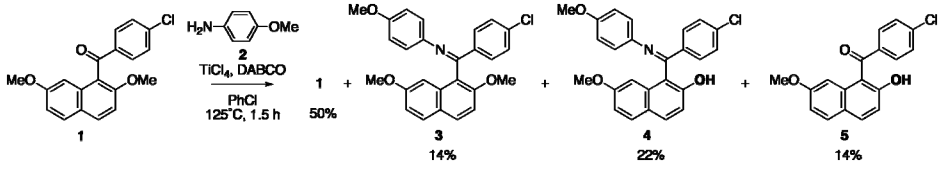
To a solution of 2,7-dimethoxynaphthalene (0.200 mmol, 68.2 mg) and 4-chlorobenzoyl chloride (0.220 mmol, 38.5 mg) in dichloromethane (0.5 mL), $AlCl_3$ (0.220 mmol, 29.3 mg) was added by portions at 0˚C under nitrogen atmosphere. After the reaction mixture was stirred at r. t. for 3 h, it was poured into iced water (20 mL) and the mixture was extracted with $CHCl_3$ (15 mL × 3). The combined extracts were washed with 2 M NaOH aq., sat. NaCl aq. and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give powdery product. The crude product of 1-momoaroylnaphthalene **1** was purified by recrystallization (hexane, isolated yield 78%).

**1-(4-Chlorobenzoyl)-2,7-dimethoxynaphthalene (1)**: Colourless needle (hexane), Mp 121.5˚C - 122˚C; IR (KBr): 1667, 1628, 1586, 1512 cm$^{-1}$; $^1$H NMR $\delta$ (300 MHz, $CDCl_3$): 7.87 (1H, d, $J$ = 9.0 Hz), 7.78 (2H, d, $J$ = 8.4 Hz), 7.72 (1H, d, $J$ = 9.0 Hz), 7.39 (2H, d, $J$ = 8.4 Hz), 7.16 (1H, d, $J$ = 9.0 Hz), 7.02 (1H, dd, $J$ = 2.4, 9.0 Hz), 6.78 (1H, d, $J$ = 2.4 Hz), 3.79 (3H, s), 3.73 (3H, s) ppm; $^{13}$C NMR $\delta$ (75 MHz, $CDCl_3$): 196.81, 158.96, 155.02, 139.71, 136.45, 132.94, 131.28, 130.87, 129.72, 128.86, 124.34, 121.06, 117.15, 110.05, 101.88, 56.239, 55.168 ppm; Calcd for $C_{19}H_{15}O_3Cl$: C, 69.83%; H, 4.63%; Found: C, 69.61%; H, 4.74%.

#### 2.2.2. $TiCl_4$—DABCO Mediated Imination of 1-(4-Chlorobenzoyl)-2,7-dimethoxynaphthalene (1)

To a solution of 1-(4-chlorobenzoyl)-2,7-dimethoxynaphthalene (**1**, 0.200 mmol, 65.4 mg) in monochlorobenzene (1 mL), mixtures of aniline (0.220 mmol, 20.5 mg), $TiCl_4$ (0.330 mmol, 62.4 mg), DABCO (1.320 mmol, 148 mg) and monochlorobenzene (1 mL) were added by portions at 90˚C under nitrogen atmosphere. After the reaction mixture was stirred at 125˚C for 1.5 h, the resulting solution was filtrated to remove the precipitate. The solvent was removed under reduced pressure to give crude material. The crude product was purified by silicagel column chromatography (Chloroform; isolated yield: imine **3**, 10%; imine **4**, 10%, 2-hydroxy compound **5**, 8%).

**Imine 3:** Colourless block ($CHCl_3$/hexane) Mp 174˚C - 175˚C, IR (KBr) 1625, 1502, 1238, 1029, 830 cm$^{-1}$; $^1$H NMR $\delta$ (300 MHz, $CDCl_3$): 7.72 (1H, d, $J$ = 9.0 Hz), 7.66 (2H, d, $J$ = 8.4 Hz), 7.60 (1H, d, $J$ = 9.0 Hz), 7.29 (2H, d, $J$ = 8.4 Hz), 7.25 (1H, d, $J$ = 9.0 Hz), 7.02 (1H, d, $J$ = 9.0 Hz), 6.92 (1H, dd, $J$ = 9.0, 2.4 Hz), 6.74 (2H, d, $J$ = 8.8 Hz), 6.68 (1H, d, $J$ = 2.4 Hz), 6.53 (2H, d, $J$ = 8.8




**Scheme 1. $TiCl_4$—DABCO mediated imination of 1-aroylated 2,7-dimethoxynaphthalene (1).**

Hz), 3.72 (3H, s), 3.70 (3H, s), 3.60 (3H, s) ppm; $^{13}$C NMR $\delta$ (75 MHz, $CDCl_3$): 163.86, 158.73, 156.27, 154.96, 144.33, 138.11, 136.46, 132.80, 130.46, 129.80, 129.51, 128.64, 124.06, 121.15, 118.58, 116.85, 113.40, 109.87, 102.72, 56.11, 55.32, 55.23 ppm; HRMS (FAB; *m*-nitrobenzyl alcohol [*m*-NBA]) m/z: $[M + H]^+$; Calcd for $C_{26}H_{23}O_3NCl$, 432.1371; Found 432.1366; Anal. Calcd for $C_{26}H_{23}O_3NCl$: C 72.15%, H 5.11%. Found: C 72.30%, H 5.13%.

**Imine 4**: Colourless block ($CHCl_3$/hexane), Mp 184˚C - 185˚C; IR (KBr) 3407, 1626, 1502, 1225, 1207, 826 $cm^{-1}$; $^1$H NMR $\delta$ (300 MHz, $CDCl_3$): 7.71 (d, $J$ = 8.8 Hz, 1H), 7.69 (d, $J$ = 8.8 Hz, 2H), 7.64 (d, $J$ = 8.8 Hz, 1H), 7.62 (d, $J$ = 9.2 Hz, 1H), 7.53 (d, $J$ = 9.2 Hz, 1H), 7.31 (d, $J$ = 8.8 Hz, 2H), 7.27 (d, $J$ = 8.8 Hz, 2H), 7.09 (d, $J$ = 8.4 Hz, 2H), 7.03 (d, $J$ = 8.8 Hz, 1H), 6.94 (dd, $J$ = 2.4, 9.2 Hz, 1H), 6.87 (d, $J$ = 7.6 Hz, 1H), 6.84 (d, $J$ = 10.0 Hz, 2H), 6.77 (dd, $J$ = 2.4, 8.6 Hz, 1H), 6.72 (m, 4H), 6.66 (d, $J$ = 2.4 Hz, 1H), 6.57 (d, $J$ = 9.2 Hz, 2H), 6.21 (d, $J$ = 2.4 Hz, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 3.64 (s, 3H), 3.20 (s, 3H) ppm; $^1$H NMR $\delta$ (300 MHz, DMSO-$d_6$): 10.01 (s, 1H), 7.67 - 7.56 (m, 5H), 7.41 (d, $J$ = 8.4 Hz, 2H), 6.97 (d, $J$ = 8.7 Hz, 1H), 6.84 - 6.75 (m, 3H), 6.57 (d, $J$ = 8.7 Hz, 2H), 6.46 (d, $J$ = 2.1 Hz, 1H), 3.59 (s, 3H), 3.52 (s, 3H) ppm; $^{13}$C NMR δ (75 MHz, $CDCl_3$): 169.19, 166.95, 162.91, 158.94, 157.82, 157.11, 157.01, 150.87, 143.50, 137.98, 137.64, 137.03, 135.45, 135.35, 135.20, 134.36, 133.38, 131.05, 130.68, 130.33, 129.88, 129.69, 129.24, 128.85, 124.55, 124.14, 123.72, 121.73, 118.59, 116.33, 116.15, 114.96, 114.52, 114.14, 113.84, 111.37, 106.53, 103.58, 55.45, 55.26, 55.24, 54.44 ppm; HRMS (FAB; *m*-NBA) m/z: $[M + H]^+$; Calcd for $C_{25}H_{21}O_3NCl$, 418.1162; Found 418.2110; Anal. Calcd for $C_{26}H_{23}O_3NCl$: C 71.97%, H 4.87%. Found: C 71.85%, H 4.82%.

**1-(4-Chlorobenzoyl)-2-hydroxy-7-methoxynaphthalene (5)**: Yellow platelet (hexane), Mp 118˚C - 118.5˚C; IR (KBr): 3434, 1623, 1583, 1513, 1214, 843 $cm^{-1}$; $^1$H NMR $\delta$ (300 MHz, $CDCl_3$): 11.35 (s, 1H), 7.85 (d, 1H, $J$ = 9.0 Hz), 7.63 (d, 1H, $J$ = 9.0 Hz), 7.58 (d, 2H, $J$ = 8.7 Hz), 7.40 (d, 2H, $J$ = 8.7 Hz), 7.07 (d, 1H, $J$ = 9.0 Hz), 6.91 (dd, 1H, $J$ = 2.4, 9.0 Hz), 6.58 (d, 1H, $J$ = 2.4 Hz), 3.37 (s, 3H) ppm; $^{13}$C NMR δ (75 MHz, $CDCl_3$): 199.1, 162.6, 158.2, 138.8, 138.7, 136.5, 133.8, 130.7, 130.2, 128.9, 123.7, 116.4, 115.8, 113.4, 106.5, 54.5 ppm; Anal. Calcd for $C_{18}H_{13}ClO_3$: C 69.13, H 4.19. Found: C 69.11, H 4.09.

**Imine 6**: Colourless block ($CHCl_3$/hexane), Mp 172˚C - 173˚C; IR (KBr): 3407, 2937, 2592, 1625, 1585, 1509, 1227 $cm^{-1}$; $^1$H NMR $\delta$ (300 MHz, DMSO-$d_6$): 10.13, (s, 1H), 7.66 - 7.60 (m, 4H), 7.44 (d, 2H), 7.00 (t, 2H), 6.95 (d, H), 6.86 - 6.76 (m, 4H), 6.52 (d, 1H), 3.64 (s, 3H), 3.29 (s, 6H) ppm; $^{13}$C NMR δ (75 MHz, DMSO-$d_6$): 164.4, 158.2, 153.7, 151.0, 137.6, 135.7, 132.2, 130.3, 130.0, 129.7, 128.7, 128.2, 123.8, 122.9, 119.2, 115.1, 115.0, 114.9, 102.6, 55.1, 47.3 ppm; HRMS (FAB; *m*-NBA) m/z: $[M + H]^+$; Calcd for $C_{24}H_{19}ClNO_2$, 388.1110; Found, 388.1104.

### 2.3. X-Ray Crystallography

For the crystal structure determination, the single-crystal of the title compounds were used for data collection on a four-circle Rigaku R-AXIS RAPID diffractometer (equipped with a two-dimensional area IP detector). The graphite-mono-chromated Cu K$\alpha$ radiation ($\lambda$ = 1.54187 Å) was used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with F2 > 2$\sigma$(F2). The data collection and cell refinement were performed using *PROCESS-AUTO* software [24]. The data reduction was performed using *CrystalStructure* [25]. The structures were solved by direct methods using *SIR*2004 [26] and refined by a full-matrix least-squares procedure using the program *SHELXL*97 [27]. All H atoms were found in a difference map and were subsequently refined as riding atoms, with the aromatic C-H = 0.95 Å and methyl C-H = 0.98 Å, and with $U_{iso}$(H) = 1.2 $U_{eq}$(C). Molecular structures of the title compounds showing the atomic numbering schemes are shown in **Figures 1** and **2**. The crystallography details for the structure determination of the compounds are displayed in **Tables 1** and **2**.

## 3. Results and Discussion

**Tables 1** and **2** show the crystallographic data of triarylimines and the precursor compounds. *C*,*C*,*N*-triarylimines were prepared by $TiCl_4$—1,4-diazabicyclo [2.2.2] octane (DABCO)-mediated imination (see Experimental section).

**Figure 1** shows single molecular structures of 1-aroyl-2,7-dimethoxynaphthalene **1** [28], imine **3**, and 1-aroyl-2-hydroxy-7-methoxynaphthalene **5** [29] in crystal.

The aroyl group of 1-aroylnaphthalene **1** is non- coplanarly attached to the naphthalene ring. The dihedral angle between the benzene ring and the naphthalene ring is 72.06(7)˚. On the other hand, 1-aroylated 2-hydroxy-7-methoxynaphthalene (**5**) has an intramolecular O-H···O=C hydrogen bond between the carbonyl group and the hydroxy substituent on the naphthalene ring system [O2-H2···O1; 2.5573(16) Å]. The angle between the C=O bond plane and the naphthalene ring system is relatively small [20.96(8)˚]. Naturally, the angle between the benzene ring and the carbonyl group is rather large [35.65(9)˚] compared to that in the original ketone compound [**1**, 3.43(11)˚], which has 2-methoxy group instead of 2-hydroxy substituent. Consequence of this, two aromatic rings in the methyl ether-*cleaved* ketone **5** make smaller dihedral angle [58.10(6)˚] than the precursory ketone compound [**1**, 72.06(7)˚] in crystal.

**Table 1. Crystallographic data and structure refinement parameters of molecule 1 and 3.**

| | **1** | **imine 3** |
|---|---|---|
| Empirical formula | $C_{19}H_{15}ClO_3$ | $C_{26}H_{22}ClNO_3$ |
| Formula weight ($g \cdot mol^{-1}$) | 326.76 | 431.90 |
| Crystal shape, colour | Platelet, colorless | Platelet, yellow |
| Melting point (K) | 296 | 447.2 - 447.7 |
| Temperature (K) | 193(2) | 193(2) |
| Radiation type | Cu *Kα* | Cu *Kα* |
| Wavelength (Å) | 1.54187 | 1.54187 |
| Crystal sytem<br>Space group | Orthorhombic<br>Pbca | Monoclinic<br>$P2_1/a$ |
| *a*, *b*, *c* (Å) | 6.6033 (3),<br>16.0751 (7),<br>130.2216 (12) | 10.8534(6),<br>20.6421(12),<br>11.1449(8) |
| ° | 90.00,<br>90.00,<br>90.00 | 90.00,<br>118.335(3),<br>90.00 |
| Volume ($Å^3$) | 3208.0(2) | 2197.7(2) |
| *Z*, Calculated density ($Mg \cdot m^{-3}$) | 8, 1.353 | 4, 1.305 |
| Absorption coefficient ($mm^{-1}$) | 2.213 | 1.761 |
| *F*(000) | 1360 | 904 |
| Crystal size (mm) | 0.40 × 0.15 × 0.10 | 0.40 × 0.40 × 0.10 |
| Theta range for data collection | 5.5˚ to 68.1˚ | 4.3˚ to 68.2˚ |
| Limiting indices | $-7 \le h \le 7$<br>$-19 \le k \le 19$<br>$-36 \le l \le 36$ | $-13 \le h \le 13$<br>$-24 \le k \le 24$<br>$-13 \le l \le 13$ |
| Reflections collected/unique | 54984/2919<br>[$R_{int}$ = 0.032] | 15973/4023<br>[$R_{int}$ = 0.127] |
| Completeness to theta (%) | 100 [68.13˚] | 99.9 [68.25˚] |
| Max. and min. transmission | 0.802 and 0.617 | 0.844 and 0.539 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 2910/0/210 | 4023/0/281 |
| Goodness-of-fit on F^2 | 1.11 | 1.01 |
| Final *R* indices [I > 2 sigma (I)] | R1 = 0.040,<br>wR2 = 0.113 | R1 = 0.074,<br>wR2 = 0.187 |
| *R* indices (all data) | R1 = 0.046,<br>wR2 = 0.118 | R1 = 0.10,<br>wR2 = 0.213 |
| Largest diff. peak and hole | 0.13 e $Å^{-3}$ and<br>−0.33 e $Å^{-3}$ | 0.44 e $Å^{-3}$ and<br>−0.36 e $Å^{-3}$ |

**Table 2. Crystallographic data and structure refinement parameters of molecule 5 and 6.**

| | **5** | **imine 6** |
|---|---|---|
| Empirical formula | $C_{18}H_{13}ClO_3$ | $C_{24}H_{18}ClNO_2 \cdot 0.5C_6H_{12}N_2$ |
| Formula weight ($g \cdot mol^{-1}$) | 312.73 | 443.93 |
| Crystal shape, colour | Platelet, yellow | Block, colorless |
| Melting point (K) | 391.0 - 391.5 | 445.6 - 446.0 |
| Temperature (K) | 123 | 193(2) |
| Radiation type | Cu *Kα* | Cu *Kα* |
| Wavelength (Å) | 1.54187 | 1.54187 |
| Crystal sytem<br>Space group | Orthorhombic<br>Pbca | Monoclinic<br>$C2/c$ |
| *a*, *b*, *c* (Å) | 17.8030 (3),<br>8.68121 (10),<br>18.8683 (3) | 25.0027(5),<br>9.92298(18),<br>20.0052(4) |
| ° | 90.00,<br>90.00,<br>90.00 | 90.00,<br>114.6210(10),<br>90.00 |
| Volume ($Å^3$) | 2916.14(8) | 4512.07(16) |
| *Z*, Calculated density ($Mg \cdot m^{-3}$) | 8, 1.425 | 8, 1.307 |
| Absorption coefficient ($mm^{-1}$) | 2.41 | 1.71 |
| *F*(000) | 1296 | 1864 |
| Crystal size (mm) | 0.60 × 0.15 × 0.05 | 0.60 × 0.50 × 0.40 |
| Theta range for data collection | 4.7˚ to 68.2˚ | 3.6˚ to 68.2˚ |
| Limiting indices | $-21 \le h \le 21$<br>$-10 \le k \le 10$<br>$-22 \le l \le 22$ | $-30 \le h \le 30$<br>$-11 \le k \le 11$<br>$-24 \le l \le 24$ |
| Reflections collected/unique | 49864/2669<br>[$R_{int}$ = 0.033] | 39753/4125<br>[$R_{int}$ = 0.026] |
| Completeness to theta (%) | 100 [68.23˚] | 100 [68.23˚] |
| Max. and min. transmission | 0.886 and 0.485 | 0.548 and 0.381 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 2669/0/205 | 40125/0/495 |
| Goodness-of-fit on F^2 | 1.08 | 1.04 |
| Final *R* indices [I > 2 sigma (I)] | R1 = 0.0328<br>wR2 = 0.0932 | R1 = 0.0341,<br>wR2 = 0.0955 |
| *R* indices (all data) | R1 = 0.0370,<br>wR2 = 0.0963 | R1 = 0.0359,<br>wR2 = 0.0969 |
| Largest diff. peak and hole | 0.17 e $Å^{-3}$ and<br>−0.25 e $Å^{-3}$ | 0.44 e $Å^{-3}$ and<br>−0.32 e $Å^{-3}$ |

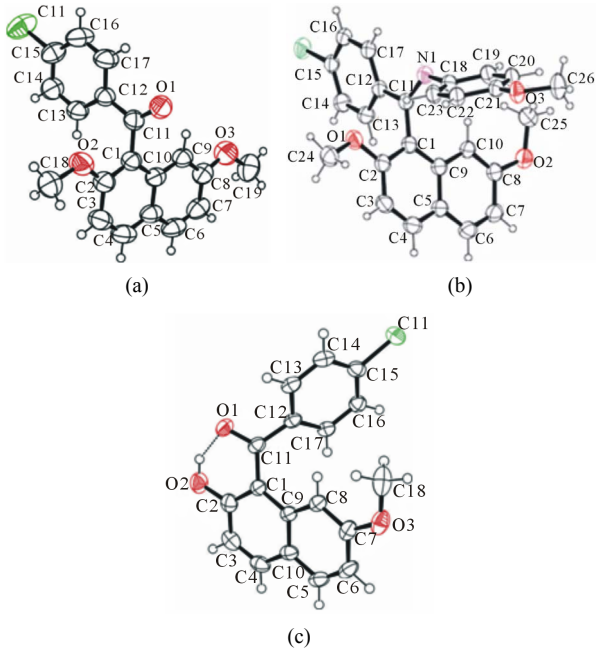



**Figure 1. Molecular structures of 1-aroyl-2,7-dimetho- xynaphthalene 1 (a), imine 3 (b), and 1-aroyl-2-hydroxy-7-methoxynaphthalene 5 (c) with the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level.**

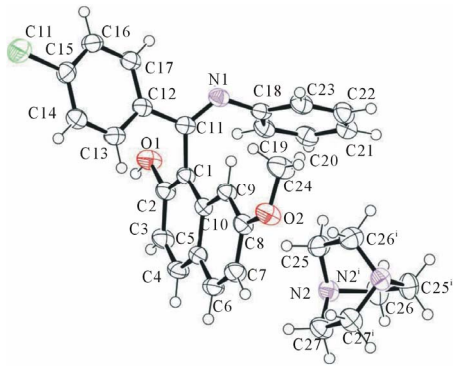


**Figure 2. Molecular structures of analogous imine 6 with the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level.**

About methyl ether-*retained* imine **3**, each of the aromatic rings is connected almost perpendicularly against both of other aromatic rings. The dihedral angles between two of the aromatic rings are close to 90˚ [85.32 (18)˚ for *C*-linked phenyl ring and naphthalene ring; 79.27(17)˚ for *N*-linked phenyl ring and naphthalene ring; 84.78(17)˚ for *C*-linked phenyl ring and *N*-linked phenyl ring, in imine **3**] compared to that of precursor 1-aroylnaphthalene **1**. These angle values indicate that three aromatic rings in methyl ether-*retained* imine **3** are situated to avoid steric hindrance to each other. However, the spatial organization of triarylimine **3** based on perpendicular arrangement of aromatic rings is essentially same to that of precursor ketone **1**.

**Figure 2** shows the single molecular structures of methyl ether-*cleaved* 1-aroylnaphthalene (**5**) originated triarylimine (**6**) [30] in crystal. Though preparation of satisfactorily qualified crystal for X-ray crystal analysis of *N*-(4-methoxyphenoxy)imine compound **4** was unsuccessful, the crystal structure of analogous imine compound (**6**) was determined. In the crystal of analogous methyl ether-*cleaved* imine **6**, two molecules of imine **6** form a 2:1 set with a DABCO molecule. However, the spatial organization of the aromatic rings in methyl ether-*cleaved* imine **6** has essentially same topology to methyl ether-*retained* imine **3**. The dihedral angles of the *C*-linked 4-chlorophenyl ring and the *N*-linked phenyl ring with the naphthalene ring are 80.39(6)˚ and 82.35 (6)˚, respectively. The dihedral angle between *C*- and *N*-linked benzene rings is 87.09(7)˚. The structural similarities between imines **3** and **6** strongly suggest that the single molecular spatial organization of three aromatic rings in perpendicular fashion is satisfactorily stable, regardless of whether triarylimine has a methoxy group at the 2-position of the naphthalene or a hydroxy one. Although both ketone **5** and imine **6** have 2-hydroxynaphthalene unit, imine **6** has molecular organization of perpendicular-based aromatic rings arrangement, which is clearly distinguishable against rather planar structure of ketone **5**.

The molecular packing of the methyl ether-*retained* imine compound **3** is compared with those of methyl ether-*retained* ketone **1** and methyl ether-*cleaved* ketone **5**. In molecular packing, 1-aroylnaphthalene **1** is mainly stabilized by van der Waals interactions. The molecules of methyl ether-*retained* ketone **1** are aligned consecutively in stacks along the *a* axis (**Figure 3**). Adjacent 4-chlorophenyl groups are exactly parallel, and the perpendicular distance between these planes is 3.660 (1) Å (**Figure 4**). **Figure 5** shows the herringbone packing of

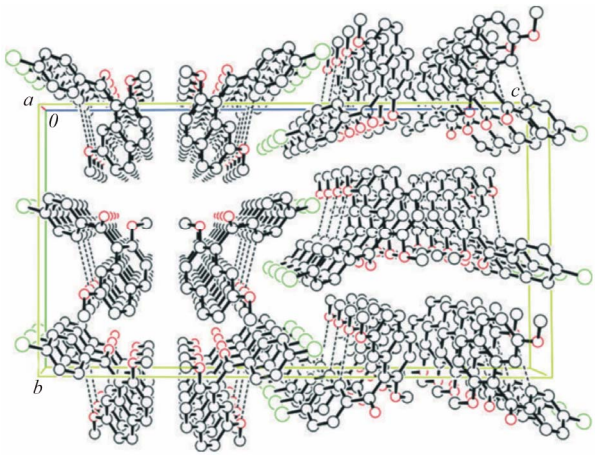



**Figure 3. The molecular alignment of 1-monoaroylnaphthalene 1, viewed along the *a* axis. H atoms are omitted.**

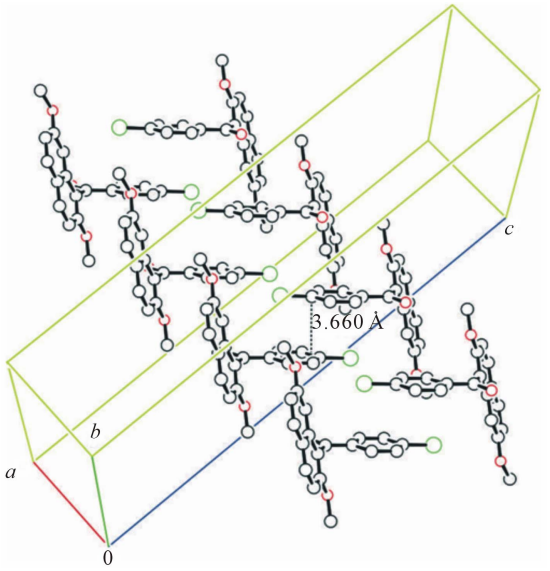



**Figure 4. The alignment of the molecule 1, viewed in an oblique direction. H atoms are omitted.**

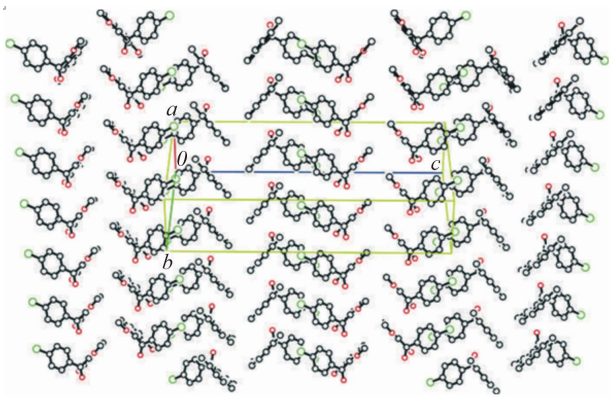



**Figure 5. The alignment of the molecule 1, showing the herringbone packing. H atoms are omitted.**

the naphthalene ring in the crystal of ketone **1**. One pile is composed of one configuration of molecule **1**. The adjacent pile is composed of the other configuration of molecule **1**. The piles of molecules are aligned alternately to vanish Cl···Cl electrostatic repulsion. The crystal packing is additionally stabilized by intermolecular (benzene)C-H···O(methoxy) hydrogen bonding between the hydrogen atom of the neighboring 4-chlorophenyl group and a methoxy oxygen of the adjacent molecule (C13-H13···O3; **Figure 3**). In the molecular packing of methyl ether-*cleaved* ketone **5**, a three-dimensional molecular network in which the alternate arrangement of *R*- and *S*-configurated compounds is formed by loose van der Waals interactions. The naphthalene rings interact with the phenyl rings [C5···C13 = 3.363 (2) Å] and the carbonyl groups [H6···O1 = 2.70 Å] along the *a*-axis. They also interact with the methyl groups [H3···C18 = 2.79 Å] and aroyl groups [H6···Cl1 = 2.88 Å] along the *c*-axis (**Figure 6**). On the other hand, the naphthalene rings also interact with the methyl groups [C6···H18B = 2.81 Å, C7···H18B = 2.70 Å] and the phenyl rings [C6···H17 = 2.88 Å, C7···H17 = 2.79 Å] along the *b*-axis. The naphthalene rings are almost perpendicular to the phenyl rings of the adjacent molecules along the *b*-axis. In addition, the hydroxy groups interact with the phenyl rings [O2···H14 = 2.71 Å] along the *b*-axis (**Figure 7**).

In the molecular packing of methyl ether-*retained* imine **3**, one *R*-configurated molecule of imine **3** and an *S*-counterpart make a pair by the aid of (*N*-phenyl) C-H···π (*C*-phenyl) interactions (C20-H20···Cg3; Cg3 is *C*-linked benzene ring of the adjacent molecule) and C-H···N (C25-H25B···N1) ones, and then the dimeric units stack along a *ac* diagonal through (*C*-phenyl) C-Cl···O (naphthalene) (C15-Cl1···O2) interactions (**Figures 8** and **9**). The tubular molecular alignments are connected by two types of C-H···O interaction (C7-H7···O3 and C14-H14···O1, **Figure 10**). According to **Table 3**, the molecular packing structures of methyl

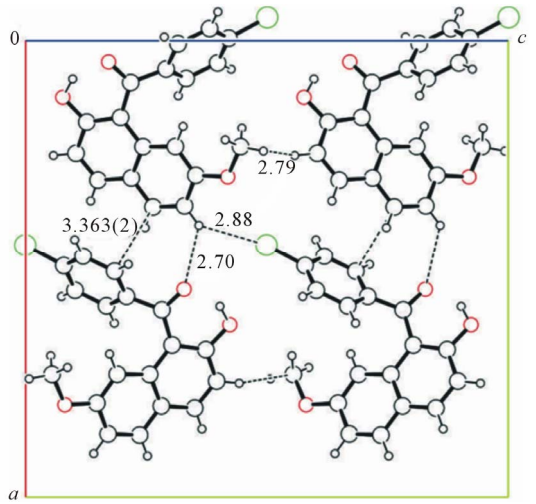



**Figure 6. A partial crystal packing diagram of compound 4, viewed down the *b*-axis (the intermolecular C-H···O and C-H···π interactions are shown as dashed lines).**

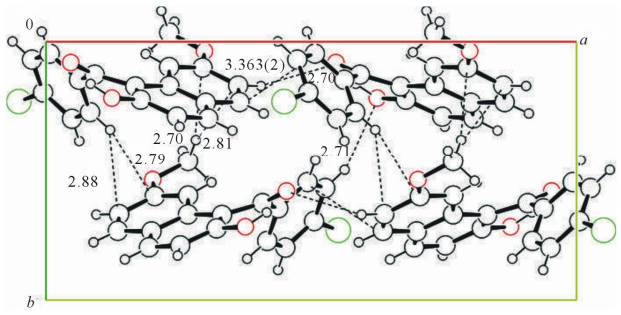



**Figure 7. A partial crystal packing diagram of compound 4, viewed down the *c*-axis (the intermolecular C-H···O and C-H···π interactions are shown as dashed lines).**

methyl ether-*retained* imine **3** are apparently directed by various kinds of effective interactions compared to the precursor ketone **1**. Especially, C-H···π and C-H···N interactions affording molecular pairs play a key role to govern the whole molecular packing. These interactions presumably maintain the spatial organization of an *R*-*S* pair of imine **3** molecules with minimized inner steric repulsions.

Methyl ether-*retained* ketone **1** has enough flexible molecular skeleton to perturb the spatial organization so that the suitable stabilized molecular stack is achieved leading the optimal molecular packing. On the other hand, the rigid conformation of methyl ether-*retained* imine **3** molecule should have little space for perturbation of configuration. As a result, predominant two interactions function within the same pair of imine **3** instead of sequential interactions resulting in formation of dimeric pairs**.** Although the semi-rigid conformation of the methyl ether-*cleaved* ketone **5** is similar to methyl ether-*retained* imine **3**, loose van der Waals interactions might restrict roughly the perturbation of configuration.

## 4. Conclusion

Conclusively, the single molecular organization of the two types of *C*,*C*,*N*-triarylimine compounds with 2- methoxy or 2-hydroxy group in crystal is displayed topologically same. The three aromatic rings are situated almost perpendicularly to each other, regardless whether triarylimine has a methoxy group at the 2-position of the naphthalene or a hydroxy one. On the other hand, the crystal structure of methyl ether-*retained* ketone clearly differs from the methyl ether-*cleaved* counterpart. There-

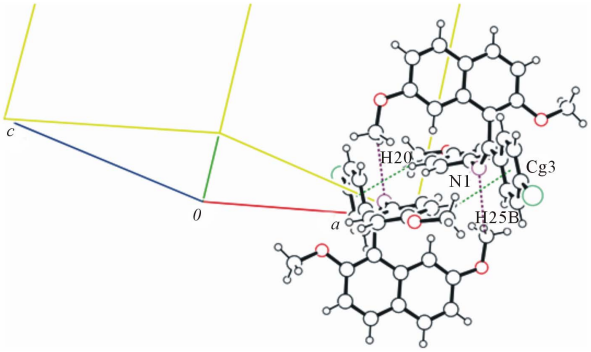



**Figure 8. Molecular pair of imine 3 by forming C-H···N and C-H···π interactions.**

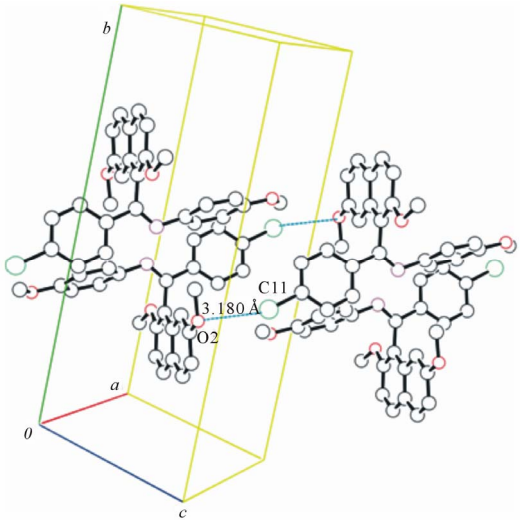



**Figure 9. Molecular alignment of imine 3 via C-Cl···O interactions, viewed in *ac* diagonal. H atoms are omitted.**

**Table 3. Crystallographic data and structure refinement parameters of molecule 1, 3, 5, and 6.**

| D-X···A | D-X | X···A | D···A | D-X···A |
|---|---|---|---|---|
| 1-aroyl-2-$OCH_3$ **1** | | | | |
| C13-H13···O3$^{i}$ | 0.93 | 2.58 | 3.401(2) | 148 |
| Imine **3** | | | | |
| C20-H20···Cg3$^{ii}$ | 0.95 | 2.90 | 3.719(4) | 145 |
| C7-H7···O3$^{iii}$ | 0.95 | 2.51 | 3.244(5) | 134 |
| C14-H14···O1$^{iv}$ | 0.95 | 2.67 | 3.525 | 150 |
| C25-H25B···N1$^{ii}$ | 0.98 | 2.70 | 3.756 | 122 |
| C15-Cl1···O2$^{v}$ | 1.739(4) | 3.180(3) | 4.795 | 153.00(15) |
| 1-aroyl-2-OH **5** | | | | |
| O2-H2···O1 | 0.94(2) | 1.71(2) | 2.5573(16) | 148(2) |
| Imine **6** | | | | |
| O1-H1···N2$^{vi}$ | 0.89 (2) | 1.86 (2) | 2.7401(18) | 167.2 (18) |
| C20-H20···Cl1$^{vii}$ | 0.95 | 2.78 | 3.6071(17) | 146 |

Symmetry code: (i) $x + 1, y, z$, (ii) $1 - x, 2 - y, 1 - z$, (iii) $-1/2 + x, 1.5 - y, -1 + z$, (iv) $-x, 2 - y, 1 - z$, (v) $-x, 2 - y, -z$, (vi) $-x + 1, -y, -z+1$, (vii) $x + 1/2, -y + 1/2, z + 1/2$.

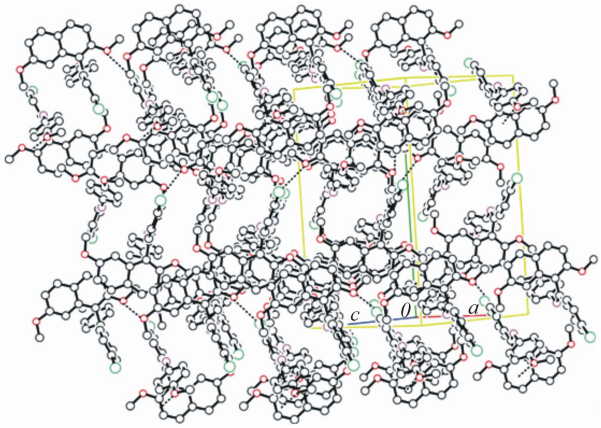



**Figure 10. Tubluar molecular alignments of imine 3, viewed down *ac* diagonal. H atoms are omitted.**

fore, triarylimine compounds have proved enough stable by the aid of the adapting of steric hindrance releasing molecular organization, where three aromatic rings situate perpendicularly to each other. The molecular packings of 1-aroyl-2,7-dimethoxynaphthalene and methyl ether-*retained* triarylimine clearly differ to each other, *i.e.*, the piles composed of one configurated molecules for the ketone and the tubular molecular alignments composed of *R*-*S* dimeric molecules for the imine. The difference is interpreted on the basis of flexibility of the molecular skeletons governing the number and the strength of effective intermolecular interactions.

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## REFERENCES

[1] A. J. Neel, J. P. Hehn, P. F. Tripet and F. D. Toste, "Asymmetric Cross-Dehydrogenative Coupling Enabled by the Design and Application of Chiral Triazole-Containing Phosphoric Acids," *Journal of American Chemical Society*, Vol. 135, No. 38, 2013, pp. 14044-14047. http://dx.doi.org/10.1021/ja407410b

[2] R. Sun, C. Xue, X. Ma, M. Gao, H. Tian and Q. Li, "Light-Driven Linear Helical Supramolecular Polymer Formed by Molecular-Recognition-Directed Self-Assembly of Bis(*p*-sulfonatocalix[4]arene) and Pseudorotaxane," *Journal of American Chemical Society*, Vol. 135, No. 16, 2013, pp. 5990-5993. http://dx.doi.org/10.1021/ja4016952

[3] B. Jose, S. Matsushita and K. Akagi, "Lyotropic Chiral Nematic Liquid Crystalline Aliphatic Conjugated Polymers Based on Disubstituted Polyacetylene Derivatives That Exhibit High Dissymmetry Factors in Circularly Polarized Luminescence," *Journal of American Chemical Society*, Vol. 134, No. 48, 2012, pp. 19795-19807. http://dx.doi.org/10.1021/ja3086565

[4] Z. Furen, S. Haibin and Z. Guofu, "Synthesis and Catalytic Activity of Group 5 Metal Amides with Chiral Biaryldiamine-Based Ligands," *Dalton Transactions*, Vol. 40, No. 7, 2011, pp. 1547-1566. http://dx.doi.org/10.1039/c0dt01229g

[5] C. Chan, N.-W. Tseng, J. Ram, J. Liu, R. Kwok and B. Tang, "Construction of Functional Macromolecules with Well-Defined Structures by Indium-Catalyzed Three-Component Polycoupling of Alkynes, Aldehydes, and Amines," *Macromolecules*, Vol. 46, No. 9, 2013, pp. 3246-3256. http://dx.doi.org/10.1021/ma4005346

[6] O. Lucchi, "High Symmetry Chiral Auxiliaries Containing Heteroatoms," *Pure and Applied Chemistry*, Vol. 68, No. 4, 1996, pp. 945-950. http://dx.doi.org/10.1351/pac199668040945

[7] K. Maruoka, "Asymmetric Phase Transfer Catalysis," Wiley-VCH, Weinheim, 2008. http://dx.doi.org/10.1002/9783527622627

[8] M. T. Scerba, C. M. Leavitt, M. E. Diener, A. F. DeBlase and T. Lectka, "$NH^+$-F Hydrogen Bonding in a Fluorinated 'Proton Sponge' Derivative: Integration of Solution, Solid-State, Gas-Phase, and Computational Studies," *Journal of Organic Chemistry*, Vol. 76, No. 19, 2011, pp. 7975-7984. http://dx.doi.org/10.1021/jo2015328

[9] S. Shinamura, E. Miyazaki and K. Takiyama, "Synthesis, Properties, Crystal Structures, and Semiconductor Characteristics of Naphtho[1,2-b:5,6-b']dithiophene and -Diselenophene Derivatives," *Journal of Organic Chemistry*, Vol. 75, No. 4, 2010, pp. 1228-1234. http://dx.doi.org/10.1021/jo902545a

[10] Z. Y. Wang and A. L. Guen, "Synthesis and Properties of Poly(arylene ether)s Containing 1,8-Dibenzoylnaphthalene Units," *Macromolecules*, Vol. 28, No. 10, 1995, pp. 3728-3732. http://dx.doi.org/10.1021/ma00114a029

[11] Y. L. Jiang, X. Gao, G. Guannan, A. Patel and A. Javer, "Selective Recognition of Uracil and Its Derivatives Using a DNA Repair Enzyme Structual Mimic," *Journal of Organic Chemistry*, Vol. 75, No. 2, 2010, pp. 324-333. http://dx.doi.org/10.1021/jo901862x

[12] X. Mei, R. M. Martin and C. Wolf, "Synthesis of Sterically Crowded Atropisomeric 1,8-Diacridylnaphthalene for Dual-Mode Enantioselective Fluorosensing," *Journal of Organic Chemistry*, Vol.71, No.7, 2006, pp. 2854-2861. http://dx.doi.org/10.1021/jo0600353

[13] S. Cohen, M. Thirumalaikumar, S. Pogodin and I. Agranat, "Peri Interactions in Naphthalene Diketones: A Preference for (Z,Z) Conformations," *Structure Chemistry*, Vol. 154, No. 4, 2004, pp. 339-346. http://dx.doi.org/10.1023/B:STUC.0000026750.39809.07

[14] L.-H. Jing, D.-B. Qin, L. He, S.-J. Gu, H.-X. Zhang and G. Lei, "Dimethyl Naphthalene-1,8-dicarboxylate," *Acta Crystallographica Section E*, Vol. 61, 2005, pp. o3595-o3596. http://dx.doi.org/10.1107/S160053680503148X

[15] A. Okamoto, S. Watanabe, K. Nakaema and N. Yonezawa, "Crystal Structure and Solution Structural Dynamic Feature of 1,8-Dibenzoyl-2,7-dimethoxynaphthalene," *Crystal Structure Theory and Applications*, Vol. 1, No. 3, 2012, pp. 121-127.

http://dx.doi.org/10.4236/csta.2012.13022

[16] P. H. Gore and K. Henrick, "1,8-Dibenzoyl-2,7-dimethylnaphthalene," *Acta Crystallographica Section B*, Vol. B36, 1980, pp. 2462-2465. http://dx.doi.org/10.1107/S0567740880009077

[17] A. Okamoto and N. Yonezawa, "Reversible $ArS_E$ Aroylation of Naphthalene Derivatives," *Chemistry Letters*, Vol. 38, No. 9, 2009, pp. 914-915. http://dx.doi.org/10.1246/cl.2009.914

[18] A. Okamoto, R. Mitsui, H. Oike and N. Yonezawa, "Lewis Acid-Mediated $ArS_E$ Aroylation of Naphthalene Derivative: Distinct Second Aroylation Behavior of Naphthyl Ketone," *Chemistry Letters*, Vol. 40, No. 11, 2011, pp. 1283-1284. http://dx.doi.org/10.1246/cl.2011.1283

[19] A. Okamoto, A. Nagasawa and N. Yonezawa, "Preparation and Structure of *C*,*C*,*N*-Triaryl Substituted Imine: $TiCl_4$-DABCO-Mediated Imination of 1-Aroyl-2,7-dimethoxynaphthalene and Spatial Organization of the Produced Imine Molecule in Crystal," 2013, in press.

[20] K. Sasagawa, R. Takeuchi, T. Kusakabe, N. Yonezawa and A. Okamoto, "{2,7-Dimethoxy-8-[4-(propan-2-yloxy)-benzoyl]naphthalen-1-yl}[4-(propan-2-yloxy)phenyl]methanone," *Acta Crystallographica Section E*, Vol. 69, 2013, pp. o444-445. http://dx.doi.org/10.1107/S1600536813004959

[21] S. Mouri, D. Hijikata, K. Isozaki, N. Yonezawa and A. Okamoto, "[2,7-Diethoxy-8-(4-fluorobenzoyl)naphthalen-1-yl](4-fluorophenyl)methanone," *Acta Crystallographica Section E*, Vol. 69, 2013, p. o637. http://dx.doi.org/10.1107/S1600536813008295

[22] S. Yoshiwaka, D. Hijikata, K. Sasagawa, N. Yonezawa and A. Okamoto, "[8-(4-Phenoxybenzoyl)-2,7-bis(propan-2-yloxy)naphthalen-1-yl](4-phenoxyphenyl)methanone," *Acta Crystallographica Section E*, Vol. 69, 2013, p. o242. http://dx.doi.org/10.1107/S1600536813000913

[23] A. Okamoto, A. Nagasawa and N. Yonezawa, "Preparation and Structure of *C*,*C*,*N*-Triaryl Substituted Imines: $TiCl_4$-1,4-Diazabicyclo[2.2.2]octane-mediated Imination of 1-Aroyl-2,7-dimethoxynaphthalene and Spatial Organization of the Produced Imine Molecule in Crystal," *European Chemical Bulletin*, Vol. 3, 2014, pp. 13-17.

[24] Rigaku, "PROCESS-AUTO," Rigaku Corporation, Tokyo, 1998.

[25] Rigaku/MSC, "CrystalStructure," Rigaku/MSC, The Woodlands, 2004.

[26] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, "*SIR*2004: An Improved Tool for Crystal Structure Determination and Refinement," *Journal of Applied Crystallography.*, Vol. 38, 2005, pp. 381-388. http://dx.doi.org/10.1107/S002188980403225X

[27] G. M. Sheldrick, "A Short History of SHELX," *Acta Crystallographica Section A*, Vol. A64, 2008, pp. 112-122. http://dx.doi.org/10.1107/S0108767307043930

[28] R. Mitsui, K. Nakaema, K. Noguchi, A. Okamoto and N. Yonezawa, "1-(4-Chlorobenzoyl)-2,7-dimethoxynaphthalene," *Acta Crystallographica Section E*, Vol. E64, 2008, p. o1278. http://dx.doi.org/10.1107/S1600536808017297

[29] R. Mitsui, K. Nakaema, K. Noguchi and N. Yonezawa, "(4-Chlorophenyl)(2-hydroxy-7-methoxynaphthalen-1-yl) methanone," *Acta Crystallographica Section E*, Vol. E64, 2008, p. o2497. http://dx.doi.org/10.1107/S1600536808039603

[30] A. Nagasawa, R. Mitsui, Y. Kato, A. Okamoto and N. Yonezawa, "1-[(4-Chlorophenyl)(phenylimino)methyl]-7-methoxy-2-naphthol-1,4-diazabicyclo[2.2.2]octane (2/1)," *Acta Crystallographica Section E*, Vol. E66, 2010, p. o2497.