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 aryl 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 aryl 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 arylnaphthalene molecules for realization of more crowded inner spatial situation in accumulated aromatic-rings molecule. As one of the molecular transformation approaches to obtain such spatial organization, the authors designed conversion of ketonic carbonyl group...
on 1-arylnaphthalene to imino moiety by the re-action with aniline derivative. Imination of 1-arylated 2,7-dimethoxynaphthalene with aromatic amines scarcely proceeded with conventional additives except for TiCl₄ and 1,4-diazabicyclo[2.2.2]octane (DABCO) mixture. In TiCl₄—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-arylated 2,7-dimethoxynaphthalene derivatives plausibly accelerates TiCl₄-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-aryl-2,7-dimethoxynaphthalene and 1-aryl-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

¹H 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 Me₂Si (δ 0.00). ¹³C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (75 MHz). Chemical shifts are expressed in ppm relative to internal standard of CDCl₃ (δ 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 AlCl₃

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), AlCl₃ (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 CHCl₃ (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; ¹H NMR δ (300 MHz, CDCl₃): 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; ¹³C NMR δ (75 MHz, CDCl₃): 196.81, 158.96, 155.02, 139.11, 136.45, 132.94, 131.28, 129.72, 128.86, 124.34, 121.06, 117.15, 110.05, 101.88, 56.239, 55.168 ppm; Calcd for C₁₉H₁₅O₃Cl: C, 69.83%; H, 4.63%; Found: C, 69.61%; H, 4.74%.

2.2.2. TiCl₄—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), TiCl₄ (0.330 mmol, 68.2 mg) and 4-chlorobenzoyl chloride (0.220 mmol, 38.5 mg) in dichloromethane (0.5 mL), AlCl₃ (0.220 mmol, 29.3 mg) was added by portions at 0°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 (CHCl₃/hexane) Mp 174°C - 175°C, IR (KBr) 1625, 1502, 1238, 1029, 830 cm⁻¹; ¹H NMR δ (300 MHz, CDCl₃): 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 Hz); ¹³C NMR δ (75 MHz, CDCl₃): 196.81, 158.96, 155.02, 139.11, 136.45, 132.94, 131.28, 129.72, 128.86, 124.34, 121.06, 117.15, 110.05, 101.88, 56.239, 55.168 ppm; Calcd for C₁₉H₁₃O₄Cl: C, 69.83%; H, 4.63%; Found: C, 69.61%; H, 4.74%.
1H NMR δ (300 MHz, DMSO-d6) : 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; 13C NMR δ (75 MHz, CDCl3) : 169.19, 166.95, 162.91, 158.94, 157.82, 157.11, 157.01, 150.87, 143.50, 138.11, 136.46, 132.80, 130.46, 130.8. 1H NMR δ (300 MHz, DMSO-d6) : 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; 13C NMR δ (75 MHz, CDCl3) : 169.19, 166.95, 162.91, 158.94, 157.82, 157.11, 157.01, 150.87, 143.50, 138.11, 136.46, 132.80, 130.46, 130.8. 

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 TiCl4—1,4-diazabicyclo[2.2.2]octane (DABCO)-mediated imination (see Experimental section).

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

The aroyl group of 1-arylnaphthalene 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    | C₁₉H₁₅ClO₃        | C₂₆H₂₂ClNO₃     |
| Formula weight       | 326.76 (g·mol⁻¹)   | 431.90           |
| Crystal shape, colour| Platelet, colorless| Platelet, yellow |
| Melting point (K)    | 193(2)             | 193(2)           |
| Radiation type       | Cu Kα              | Cu Kα            |
| Wavelength (Å)       | 1.54187            | 1.54187          |
| Crystal system       | Orthorhombic       | Monoclinic       |
| Space group          | Pbc/a              | Pbca             |
| a, b, c (Å)          | 6.6033 (3), 16.0751 (7), 130.2216 (12) | 10.85346, 20.6421 (12), 11.14498 (8) |
| Z                     | 90.00, 90.00, 90.00 | 118.335 (3), 90.00 |
| Volume (Å³)          | 3208.0 (2)         | 2197.7 (2)       |
| 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 ≤ h ≤ 7, -13 ≤ k ≤ 13, -36 ≤ l ≤ 36 | -19 ≤ h ≤ 19, -24 ≤ k ≤ 24, -36 ≤ l ≤ 36 |
| Reflections collected/unique | 54984/2919 | 15973/4023 |
| R/ω (%)              | 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 F² | Full-matrix least-squares on F² |
| Data/restraints/parameters | 2910/0.210 | 4023/0.281 |
| Goodness-of-fit on F² | 1.11              | 1.01             |
| Final R indices [I > 2 sigma (I)] | R₁ = 0.040, wR₂ = 0.113 | R₁ = 0.074, wR₂ = 0.187 |
| R indices (all data) | R₁ = 0.046, wR₂ = 0.118 | R₁ = 0.10, wR₂ = 0.213 |
| Largest diff. peak and hole | 0.13 e Å⁻³ and −0.33 e Å⁻³ | 0.44 e Å⁻³ and −0.36 e Å⁻³ |

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

|                      | 5                  | imine 6          |
|----------------------|--------------------|------------------|
| Empirical formula    | C₁₈H₁₃ClO₃        | C₂₄H₁₈ClNO₂·0.5C₆H₁₂N₂ |
| Formula weight       | 312.73 (g·mol⁻¹)   | 443.93           |
| Crystal shape, colour| Platelet, yellow   | Block, colorless |
| Melting point (K)    | 391.0 - 391.5      | 445.6 - 446.0    |
| Radiation type       | Cu Kα              | Cu Kα            |
| Wavelength (Å)       | 1.54187            | 1.54187          |
| Crystal system       | Orthorhombic       | Monoclinic       |
| Space group          | Pbc/a              | Pbca             |
| a, b, c (Å)          | 17.8030 (3), 8.68121 (10), 18.8683 (3) | 25.0027 (5), 9.92298 (18), 20.0052 (4) |
| Z                     | 90.00, 90.00, 90.00 | 114.6210 (10), 90.00 |
| Volume (Å³)          | 2916.14 (8)        | 4512.07 (16)     |
| 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 ≤ h ≤ 21, -30 ≤ h ≤ 30 | -11 ≤ k ≤ 11, -24 ≤ l ≤ 24 |
| Limiting indices     | -10 ≤ k ≤ 10, -11 ≤ k ≤ 11 | -22 ≤ l ≤ 22 |
| Reflections collected/unique | 49864/2669 | 39753/4125 |
| R/ω (%)              | 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 F² | Full-matrix least-squares on F² |
| Data/restraints/parameters | 2669/0.205 | 40125/0.495 |
| Goodness-of-fit on F² | 1.08              | 1.04             |
| Final R indices [I > 2 sigma (I)] | R₁ = 0.0328 | R₁ = 0.0341, wR₂ = 0.0955 |
| R indices (all data) | R₁ = 0.0370, wR₂ = 0.0963 | R₁ = 0.0359, wR₂ = 0.0969 |
| Largest diff. peak and hole | 0.17 e Å⁻³ and −0.25 e Å⁻³ | 0.44 e Å⁻³ and −0.32 e Å⁻³ |
Figure 1. Molecular structures of 1-aroyl-2,7-dimethoxy-naphthalene 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 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.
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-C11···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 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-C11···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 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-C11···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 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-C11···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 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).
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.

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-aryl-2-OCH₃ 1  |      |            |       |       |
| C13-H13⋯O3      | 0.93 | 2.58       | 3.401(2) | 148   |
| Imine 3         |      |            |       |       |
| C20-H20⋯Cg3     | 0.95 | 2.90       | 3.719(4) | 145   |
| C7-H7⋯O3       | 0.95 | 2.51       | 3.244(5) | 134   |
| C14-H14⋯O1      | 0.95 | 2.67       | 3.525  | 150   |
| C25-H25B⋯N1     | 0.98 | 2.70       | 3.756  | 122   |
| C15-C11⋯O2     | 1.739(4) | 3.180(3) | 4.795  | 153.00(15) |
| 1-aryl-2-OH 5   |      |            |       |       |
| O2-H2⋯O1       | 0.94(2) | 1.71(2) | 2.5573(16) | 148(2) |
| Imine 6         |      |            |       |       |
| O1-H1⋯N2       | 0.89 (2) | 1.86 (2) | 2.7401(18) | 167.2 (18) |
| C20-H20⋯C11     | 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.
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-aryl-2,7-dimethoxynaphthalene and methyl ethyl-retained triarylimine clearly differ to each other, i.e., the piles composed of one configured 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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