PREPARATION AND STRUCTURE OF C,C,N-TRIARYL SUBSTITUTED IMINE:
TiCl₄–1,4-DIAZABICYCLO[2.2.2]OCTANE-MEDIATED IMINATION OF 1-ARYL-2,7-DIMETHOXYNAPHTHALENE AND SPATIAL ORGANIZATION OF THE PRODUCED IMINE MOLECULE IN CRYSTAL

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Introduction

Non-coplanarly organized aromatic-rings accumulating compounds, e.g., biphenyls and binaphthyls, have been demonstrated as unique building blocks in construction for many functional materials.¹⁻¹⁸ Thus, organic reaction affording novel molecular motifs of non-coplanarly organized aromatic-rings accumulating compounds with minute spatial structural characterization have attracted attention of the chemists in the wide range of organic molecular science and polymer materials fields. Recently, the authors have reported specific and characteristic electrophilic aromatic aroylation of naphthalene derivatives. In this reaction, two aryl groups are regioselectively and effectively introduced at the 1,8-positions of the naphthalene ring accompanying with acid-mediated retroarylation.² The 1-monoarylated naphthalenes, which correspond to the intermediates in the diarylation, are also obtained by choice of acidic mediator.¹⁰ According to X-ray crystal structure analyses, the aryl groups in these peri-arylated naphthalene compounds are attached in a non-coplanar fashion to the naphthalene rings.¹¹⁻¹⁵ In a natural consequence, the authors have planned introduction of additional aromatic ring planes to the core of the aryl substituted naphthalene molecules to realize more crowded inner spatial situation in aromatic-rings accumulating molecule. As one of the molecular transformation approaches to obtain such spatial organization, the authors designed conversion of ketonic carbonyl group in 1-monoarylnaphthalene to imino moiety by the reaction with aromatic amines. This attempt has led the authors to reveal novel reaction behaviour of peri-arylated 2,7-dimethoxynaphthalene derivatives and the unique spatial organization of the resulting imine compounds in crystal. Herein, the authors report imination reaction of 1-monoarylnaphthalene with aromatic amine, i.e., introduction reaction of the third aromatic ring to a naphthalene molecule of non-coplanarly organized two-aromatic-rings accumulating structure and discuss the reaction mechanism. In addition, the authors introduce the spatial organization features of the resulting triarylimine molecule.

Results and discussion

Table 1 shows the results of reaction of 1-(4-chlorobenzoyl)-2,7-dimethoxynaphthalene (1) with p-anisidine (2). When molecular sieves 4Å was added, no reaction proceeded (entry 2) as well as the reaction without additive compounds (entry 1). In p-toluenesulfonic acid (TsOH)-mediated reaction,¹⁵ imine 3 was slightly obtained with recovery of starting material 1 (entry 3). TiCl₄–1,4-diazabicyclo[2.2.2]octane (DABCO)-mediated reaction¹⁶ moderately afforded imine 3 (14 %) in a similar manner of TsOH-mediated one, whereas the reaction also gave the methyl–oxygen bond cleaved species, i.e., imine 4 (22 %) and 1-monoaroylnaphthalene 5 (14 %) (entry 4).

![Table 1](image)

*Reaction conditions: 1-(4-chlorobenzoyl)naphthalene (1, 1.0 mmol), p-anisidine (2, 1.1 mmol), chlorobenzene (5 mL). *Calculated on the basis of ¹H NMR spectra. Isolated yields are given in parentheses. *MS4A (100
There are two possible reaction routes for imine 4, i.e., methyl-oxygen bond cleavage reaction of imine 3 and imination of 2-hydroxy-7-methoxy-1-monoaroylnaphthalene 5 (Scheme 1). Imine 3 formed no ether-cleaved products by treatment with TiCl₄-DABCO mixture (Scheme 2).

On the other hand, the methyl ether-cleaved 1-monoaroylnaphthalene 5 was transformed into imine 4 in a high yield (79%) when TiCl₄, DABCO, and amine 2 were treated as entry 4 in Table 1 (Scheme 3). These results strongly indicate that imine 4 was formed via the latter reaction route. In other words, imination of 1-monoaroylated 2-hydroxy-7-methoxynaphthalene 5 readily proceeds than that of the parent compound, 1-monoaroylated 2,7-dimethoxynaphthalene 1. 1-Monoaroylnaphthalene 1 was converted quantitatively to the methyl ether-cleaved 1-monoaroylnaphthalene 5 by the aid of TiCl₄-DABCO mixture in the absence of amines (Scheme 4). On the contrary, no reaction occurred by the same treatment of 2,7-dimethoxynaphthalene (Scheme 5). Furthermore, reaction of 1-monoaroylnaphthalene 1 in monochlorobenzene at 125°C for 1.5 h with TiCl₄ yielded 1-monoaroylnaphthalene 5 (75%) and 2,7-dimethoxynaphthalene 6 (25%), whereas that with DABCO formed no products (Scheme 6).
heteroatoms of the substituents to titanium atom.\textsuperscript{17}

Scheme 7

Scheme 7 well-explains the plausible reaction mechanism. The TiCl\(_4\)-DABCO-mediated imination of 1-monoaroylnaphthalene \(\text{I}\) to imine \(\text{3}\) presumably proceeds via three steps: 1) the carbonyl oxygen coordinates to titanium atom of TiCl\(_4\), 2) nucleophilic attack of the nitrogen atom of aniline to TiCl\(_4\)-activated ketonic carbonyl group of 1-monoaroylnaphthalene \(\text{I}\) proceeds with simultaneous abstraction of proton from the adduct by DABCO, and 3) deprotonation from nitrogen atom of hemiaminal forms imino moiety.

As the carbonyl carbon atom of 1-monoaroylnaphthalene \(\text{I}\) is sterically hindered, the second step of nucleophilic attack of amine is considered essentially rate-determining step for total imination reaction. So, the aryl group-assisted methyl ether-cleavage reaction of 1-monoaroylnaphthalene \(\text{I}\) presumably undergo with comparable susceptibility as well as the nucleophilic attack of the amine \(\text{2}\) to the ketonic carbonyl carbon. As the attack of amine \(\text{2}\) to the carbonyl carbon of methyl ether-cleaved-1-monoaroylnaphthalene \(\text{5}\) thus obtained should be less affected by steric hindrance than the parent compound \(\text{I}\), it smoothly affords imine \(\text{4}\).

Figure 1 displays the crystal structure of analogous imine \(\text{7}\), which has no methoxy group on the \(N\)-linked benzene. In the crystal of analogous imine \(\text{7}\), two molecules of imine \(\text{7}\) form a \(2:1\) set with a DABCO molecule. Each of the aromatic rings is connected almost perpendicularly against two other aromatic rings. The dihedral angles of the \(C\)-linked 4-chlorophenyl ring and the \(N\)-linked phenyl ring with the naphthalene ring are 80.39(6)\(^\circ\) and 82.35(6)\(^\circ\), respectively. The dihedral angle between \(C\)- and \(N\)-linked benzene rings is 87.09(7)\(^\circ\).

![Figure 1. Molecular structure of analogous imine 7, with the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level [Symmetry code (i)1-x,y, 3/2-z].](image)

Conclusively, TiCl\(_4\)-DABCO-mediated imination of 1-monoaroylated 2,7-dimethoxynaphthalene successfully yield \(C,C,N\)-aryl substituted imine compounds with/without cleavage of 2-positioned methoxy group. In crystal of an imine compound, the three aromatic rings are situated perpendicularly to each other realizing stable spatial organization.

**Experimental**

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

**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\(_4\)Si (\(\delta\) 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.

**X-ray Crystallography**

For the crystal structure determination, the single-crystal of the compound \(\text{C}_{29}\text{H}_{18}\text{ClNO}_2\cdot0.5\text{C}_8\text{H}_2\text{N}_2\) was used for data collection on a four-circle Rigaku RAXIS 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 \(F^2>2\sigma(F^2)\). The data collection and cell refinement were performed using \textit{PROCESS-AUTO} software. The data reduction was performed using \textit{CrystalStructure}. The structures were solved by direct methods using \textit{SIR2004} and refined by a full-matrix least-squares procedure using the program \textit{SHELXL97}. 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 \(U_{iso}(H) = 1.2U_{eq}(C)\).

**Synthetic procedures of 1-(4-chlorobenzoyl)-2,7-dimethoxy-naphthalene (1)**

To a solution of 2,7-dimethoxynaphthalene (6, 0.200 mmol, 68.2 mg) and 4-chlorobenzoyl chloride (0.22 mmol, 38.5 mg) in dichloromethane (0.5 mL), AlCl\(_3\) (0.22 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 aq. NaOH, saturated aq. NaCl and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give powdery product. The crude product was purified by recrystallization (hexane, isolated yield 78 %).

1-(4-Chlorobenzoyl)-2,7-dimethoxynaphthalene (1)

Colourless needles (hexane), Mp 121.5–122 °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, 139.71, 136.45, 132.94, 131.28, 130.87, 129.72, 128.86, 124.34, 121.06, 117.15, 110.05, 101.88, 56.23, 55.16 ppm; Calc'd for C₁₉H₁₃O₂Cl: C, 69.83%; H, 4.63%; Found: C, 69.61%; H, 4.74%.

Imination of 1-(4-chlorobenzoyl)-2,7-dimethoxynaphthalene (1)

To a solution of 1-(4-chlorobenzoyl)-2,7-dimethoxynaphthalene (1, 0.2 mmol, 65.4 mg) in monochlorobenzene (1 mL), mixtures of aniline (0.22 mmol, 20.5 mg), TiCl₄ (0.33 mmol, 62.4 mg), DABCO (1.32 mmol, 148.0 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 filtered 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 %).

Spectral data and elemental analyses

Imine 3

Colourless blocks (CHCl₃/hexane) Mp 174–175 °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, J = 8.8 Hz), 3.72 (3H, s), 3.70 (3H, s), 3.60 (3H, s) ppm; ¹³C NMR δ (75 MHz, CDCl₃): 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]⁺; Calc'd for C₂₆H₂₂O₂NCl: 432.1371; Found 432.1366; Anal. Calc'd for C₂₆H₂₂O₂NCl: C 72.15%, H 5.11%. Found: C 72.30%, H 5.13%.

Imine 4

Yellow platelets (hexane), Mp. 118–118.5 °C; IR (KBr): 3434, 1623, 1583, 1513, 1214, 843 cm⁻¹; ¹H NMR δ (300 MHz, CDCl₃): 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 (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; ¹³C NMR δ (75 MHz, CDCl₃): 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; Calc'd for C₁₉H₁₅O₂NCl: C 71.97 %, H 4.87 %. Found: C 71.85 %, H 4.82 %

1-(4-Chlorobenzoyl)-2-hydroxy-7-methoxynaphthalene (5)

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