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Crystal structure of 7-methoxy-1-{[(*E*)-2,6-dimethylphenylimino](phenyl)methyl}-2-naphthol: Clarification of non-covalent bonding interactions on the basis of spatial organization of single molecular structure and the molecular alignments

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ABSTRACT

Crystal structure of the title compound, 7-methoxy-1-{[(*E*)-2,6-dimethylphenylimino](phenyl)methyl}-2-naphthol, which has *N*-aryl group instead of ketonic carbonyl group has been comparatively analysed with the precursor compound of 1-benzoyl-2-hydroxy-7-methoxynaphthalene. The distinct features in the molecular accumulation structures of title triarylimine compound and the precursor diaryl ketone demonstrate that the spatial organization of the former is mainly determined π-π stacking interaction and for the latter the non-classical hydrogen bondings govern the spatial organization. Besides both of the compounds show non-coplanaryl accumulation of aromatic rings molecular structure, the title compound has molecular core of imino group which attaches three aromatic rings of *C*-1-naphthyl, *C*-phenyl, and *N*-phenyl stems of nearly perpendicular alignment of each aryl groups to residual two aryl ones respectively, giving highly congested circumstance at the inner site of molecules. On the other hand, the precursor aromatic ketone molecule has relatively large space compared to title compound, enabling conformational flexibility to some extent within restriction of maintaining non-coplanar organization. The molecules of the precursor compound in crystal are stabilized by a number of non-covalent bonding interactions, mainly by non-classical hydrogen bondings. The achievement stabilization contributed a number of non-classical hydrogen bonding is considered to be due to the inner-molecular motility of single molecular structure. Contrarily, the congested inner-molecular situation of title compound makes largely rigid molecular conformation, which affords at the same time exposure of three aromatic planes outside the molecular core. The single molecular organization permits π-π stacking interaction stabilization instead of formation of a number of weak interactions. Thus, the governing factors for the distinct feature of the single molecular and the accumulation structures of title compound and the precursor are interpreted from the viewpoint of predominantly effective intermolecular interaction, a strong π-π stacking interaction or sum of weak non-classical hydrogen bondings, determined by the inner-molecular congestive conditions directly affects the inner-molecular motility.

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1. Introduction

Understanding the nature of non-covalent bonding interactions is important for designing catalysts, organic reactions, and supramolecules [1-7]. However, flexibility of molecular structure often disturbs to grasp origin and role of respective non-covalent bonding interactions [8,9]. In organic crystals, organic molecules are aggregated through various non-covalent bonding interactions. Classical-hydrogen bonds where the hydrogen atom is bound to electronegative atoms including halogen, nitrogen, and oxygen are regarded as the strongest non-covalent bonds. π-π Stacking interactions are also effective for coplanarly-accumulated aromatic rings. On the other hands, study on non-classical hydrogen bonds where the hydrogen atom is bound to carbon have limited even though all of organic compounds have C-H bonds. The weak hydrogen bonds are plausibly hidden by strong hydrogen bonding interactions. As a natural consequence, exclusion or diminution of classical hydrogen bonding and inhibition of π-π stacking interactions are expected to unveil the latent weak interactions. From this point of view, the naphthalene derivatives having aroyl groups at *peri*-positions, *i.e.*, 1-aroyl- and 1,8-diaroylnaphthalene derivatives, are one of the good models for analysing non-covalent bonding interactions in crystal. Recently, the authors have found highly effective diaroylation at *peri*(1,8)-positions of 2,7-dialkoxynaphthalene [10,11]. Furthermore, functional group interconversion of 2- and/or 7-alkoxy group to hydroxyl group is also achievable [12]. According to X-ray crystal structure analyses, the aroyl groups in these *peri*-aroylated naphthalene compounds are attached in a non-coplanar fashion to the naphthalene rings [13-15].

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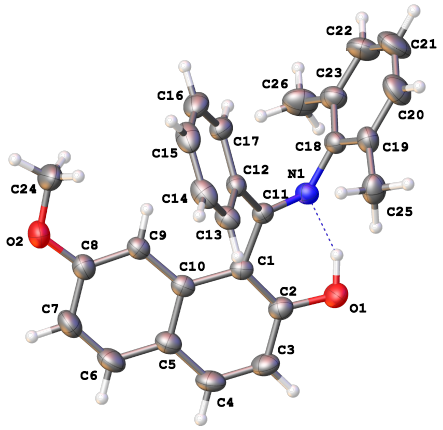

Figure 1. The molecular structure of 7-methoxy-1-{[(*E*)-2,6-dimethylphenylimino](phenyl)methyl}-2-naphthol with atom-labelling scheme. Displacement ellipsoids drawn at the 50% probability level for non-H atoms. The dotted line represents intramolecular hydrogen bond.

In molecular packing of *peri*-aroylated naphthalene compounds, four kinds of non-covalent bonding interactions, (sp^2)C-H···O=C hydrogen bond, (sp^3)C-H···O hydrogen bond, C-H···π hydrogen bonding interaction, and π-π stacking interaction are observed as the determining factors of molecular spatial organization in decreasing order of frequency [16]. In other words, *peri*-aroylated naphthalene compounds are one of the potential candidates for exteriorization of weak and moderate hydrogen bonding interactions in their crystals. In order to accomplish the purpose, the authors have planned introduction of additional aromatic ring planes to the core of the aroylnaphthalene 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-monoaroylnaphthalene to imino moiety by the reaction with aromatic amines [17,18]. Herein, the authors report crystal structure of novel triarylimine molecule, and discuss correlation among spatial structure of single molecule, non-covalent bonding interactions, and molecular accumulation structure by comparison with the precursor 1-monoaroylnaphthalene [19].

2. Experimental

2.1. Materials and methods

All reagents were of commercial quality and were used as received. Solvents were dried and purified using standard procedures [20]. Synthetic methods and spectral data for 1-benzoyl-2-hydroxy-7-methoxynaphthalene [19] have been reported in literature.

2.2. Measurements

^{1}H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (300 MHz). Chemical shifts are expressed in ppm relative to internal standard of Me_4Si (δ 0.00 ppm). ^{13}C NMR spectra were recorded on a JEOL ECX400 spectrometer (100 MHz). Chemical shifts are expressed in ppm relative to internal standard of $CDCl_3$ (δ 77.0 ppm). IR spectra were recorded on a JASCO FT/IR-4100 spectrometer (KBr tablet). High-resolution FAB mass spectra were recorded on a JEOL MStation (MS700) ion trap mass spectrometer in positive ion mode (matrix: *m*-nitrobenzyl alcohol).

2.3. X-ray crystallography

For the crystal structure determination, the single-crystal of title compound was used for data collection on a four-circle Rigaku RAXIS RAPID diffractometer (equipped with a two-dimensional area IP detector). The graphite-monochromated Mo Kα radiation (λ = 0.71075 Å) was used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2>2\theta$ (F^2).

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms could be located in difference Fourier maps, but were subsequently refined in optimized positions as riding atoms, with C-H = 0.95 (aromatic) and 0.98 (methyl) and with U_{iso}(H) = 1.2 U_{eq}(C). For data collection: *PROCESS-AUTO* [21]; cell refinement: *PROCESS-AUTO* [21]; data reduction: *CrystalStructure* [22]; program(s) used to solve structure: *SIR2004* [23]; program(s) used to refine structure: *SHELXL97* [24]; molecular graphics: *ORTEPIII* [25]. The hydrogen bond geometries of title compound are listed in Table 2 (Figure 1).

Table 1. Crystallographic data and structure refinement parameters.

Crystal data	
Chemical formula	$C_{26}H_{23}NO_2$
M_r	381.45
Crystal shape, colour	Platelet, yellow
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	193
a (Å)	8.8607(7)
b (Å)	11.6508 (10)
c (Å)	19.5234 (15)
β (°)	92.748(3)
V (Å^3)	2013.2(3)
Z	4
Radiation type	MoKα
μ (mm^{-1})	0.08
Crystal size (mm)	0.60 × 0.40 × 0.20
Data collection	
Diffractometer	Rigaku R-AXIS RAPID diffractometer
Absorption correction	Numerical NUMABS
T_{min}, T_{max}	0.954, 0.984
No. of measured, independent and observed [I > 2σ(I)] reflections	31977, 4610, 4126
R_{int}	0.019
(sin θ/λ)max (Å^{-1})	0.649
Refinement	
R[F^2 > 2σ(F^2)], wR(F^2), S	0.039, 0.114, 1.06
No. of reflections	4610
No. of parameters	292
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, -0.16
CCDC no.	1524658

Table 2. Hydrogen bond geometry (Å, °).

	D-H	H···*A*	*D*...A	*D*—H···*A*
O1-H1...N1 [i]	0.952(17)	1.686(17)	2.5586(11)	150.7(16)

Symmetry codes: (i) *x*, *y*, *z*.

Table 3. Non-covalent bonding interactions in title compound and the homologous compound (Å)

Non-covalent bonding interactions		Homologue	Title compound
Intramolecular interactions	O-H...N=C (Intra)	-	1.69
	O-H...O=C (Intra)	1.77	-
Intermolecular interactions	O-H...O=C	2.32	-
	(naph) C-H...π (naph)	2.59	-
	(benzene) C-H...π (naph)	2.96	-
	(benzene) π...π (benzene)	4.05	4.89
	(naph) π...π (naph)	-	3.70

2.4. Synthesis of title compound

To a solution of 1-benzoyl-2-hydroxy-7-methoxynaphthalene (1.0 mmol, 280 mg) in chlorobenzene (5 mL), a mixture of 2,6-dimethylaniline (1.1 mmol, 130 mg), titanium tetrachloride (1.65 mmol, 0.18 mL), 1,4-diazabicyclo[2.2.2]octane (6.6 mmol, 740 mg), and chlorobenzene (5 mL) was added by portions at 90°C under a nitrogen atmosphere. After the reaction mixture was stirred at 125°C for 12 h, the resulting mixture was filtered to remove precipitates. The filtrate was washed with saturated aqueous solution of sodium hydrogen carbonate and with brine successively. The organic layer thus obtained was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give a cake. The crude material was purified by column chromatography (silica gel, chloroform) and recrystallization from hexane (isolated yield 20%, yellow platelet, melting point 143-145 °C).

7-Methoxy-1-{[(*E*)-2,6-dimethylphenylimino](phenyl) methyl}-2-naphthol: Color: Yellow plate. Yield: 20%. M.p.: 143-145 °C. FT-IR (KBr, ν, cm^{-1}): 3433 (OH) (br, alcohol), 2992 (CH_3), 2954 (OCH_3), 1622 (C=N), 1561 (Ar), 1515 (Ar), 1239 (Ar-C-OH), 1223 (N-CAr), 1037 (Ar-O-CH_3). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.11 (s, 6H, Ar-CH_3), 3.13 (s, 3H, OCH_3), 6.33 (d, *J* = 2.4 Hz, 1H, naphthalene-H), 6.79 (dd, *J* = 8.9 Hz, 1H, naphthalene-H), 6.87-6.97 (m, 3H, 2,6-dimethylphenyl-H), 7.05-7.29 (m, 6H, phenyl-H, naphthalene-H), 7.57 (d, *J* = 8.9 Hz, 1H, naphthalene-H), 7.76 (d, *J* = 8.9 Hz, 1H, naphthalene-H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 171.3 (1C, C=N), 163.8 (1C, Ar-C-OMe), 157.5 (1C, Ar-C-OH), 144.9 (2C, Ar-CH_3), 138.0 (1C, Ar-C), 134.3 (1C, Ar-C), 134.2 (1C, Ar-C), 130.0 (2C, Ar-C), 129.4 (2C, Ar-C), 128.4 (2C, Ar-C), 128.2 (1C, Ar-C), 127.8 (2C, Ar-C), 124.3 (1C, Ar-C), 123.7 (1C, Ar-C), 117.6 (1C, Ar-C), 114.7 (1C, Ar-C), 111.8 (1C, Ar-C), 106.0 (1C, Ar-C), 54.4 (1C, OCH_3), 18.8 (2C, Ar-C-CH_3). HRMS (FAB, *m/z*): $[M + H]^+$ calcd. for $C_{26}H_{24}NO_2$, 382.1807; found, 382.1816.

3. Results and discussion

In the title molecule, the imine moiety has three types of aromatic rings, namely, a naphthalene ring (C1-C10), a phenyl ring (C12-C17) attached to carbon atom (C11), and 2,6-dimethylphenyl ring (C18-C23) attached to nitrogen atom (N1) (Figure 1). Each aromatic ring attaches in a twisted mode against other rings with almost the same level. Interplanar angles of the benzene ring and the 2,6-dimethylphenyl ring against the naphthalene ring are 75.22 (5)° and 67.54 (4)°, respectively. Furthermore, the interplanar angle between the *C*-phenyl and the *N*-(2,6-dimethyl)phenyl rings is 61.98 (6)°. Two benzene rings are situated on the same side against C=N moiety (*E* configuration). The intramolecular O-H···N=C hydrogen bond between hydroxy group at 2-position of the naphthalene ring and the imine moiety forms a six-membered ring [O1-H1···N1 = 1.686 (17) Å].

In the crystal structure, the molecular packing of the title compound is mainly stabilized by van der Waals interaction (Figure 2). In addition, two types of π-π stacking interaction alternately link the molecules into a ribbon structure along *c*-axis, *i.e.*, π-π stacking interactions between the naphthalene rings (C1-C10) and those between the 2,6-dimethylbenzene rings (C18-C23) [*Cg*...*Cg* distance: 3.699 and 4.889 Å, respectively]. The ribbons are arranged along *a*-axis, forming a sheet parallel to the *ac* plane. However, there are no effective interactions between ribbons.

Crystal structure of 1-benzoyl-2-hydroxy-7-methoxy-naphthalene, the precursor of the title compound, has reported by authors' group (Figure 3) [19]. Dihedral angle between the naphthalene ring and the phenyl ring is smaller than that of title compound [58.65(5)° *vs.* 75.22(5)°]. The precursor compound, in its crystal, also has an intramolecular O-H···O=C hydrogen bond between hydroxy group at 2-position of the naphthalene ring and the carbonyl moiety forming a six-membered ring [O1-H1···O3 = 1.77(2) Å]. The hydroxy groups form intermolecular O...H...O...H four-membered ring with adjacent molecules. The square-like classical hydrogen bonding interactions link two molecules into a head-to-head type dimeric molecular aggregate. In the molecular packing structure, the dimeric molecular aggregates arranged in an opposite orientation along *c*-axis are connected to each other by π-π stacking interactions between benzene rings forming a waving sheet structure. The layers are piled along *ac*-diagonal through two types of C-H...π hydrogen bonding interactions, *i.e.*, (benzene) C-H...π (naphthalene) and (naphthalene) C-H...π (naphthalene). The dihedral angle between the naphthalene ring and the phenyl ring is 58.65(5)°.

Both of title compound and the precursor have intramolecular classical hydrogen bonding interactions (Table 3). However, their roles in respective molecular packing seem to be distinctly different. In the precursor, intramolecular O-H...O=C classical hydrogen bond lead to intermolecular square-like O...H...O...H classical hydrogen bonds forming a dimeric molecular aggregate. The dimeric molecular aggregates are linked three-dimensionally *via* several kinds of non-classical hydrogen bonds and π-π stacking. On the other hand, the title molecules are one-dimensionally arranged into a ribbon structure through π-π stacking interactions solely.

These results can be interpreted as follows: Intramolecular N...H-O hydrogen bond in the title compound shows no effectiveness for leading non-classical hydrogen bonds to form three-dimensionally molecular network. The intramolecular hydrogen bond just contributes to stabilize spatial organization of title molecule for minimizing the internal steric repulsion. The spatial alignment of three aromatic rings accumulation is difficult to form effective intermolecular hydrogen bonds, because of their small flexibility. On the other hand, the aromatic ring moieties in precursor compound have satisfactory flexibility to make several intermolecular interactions.

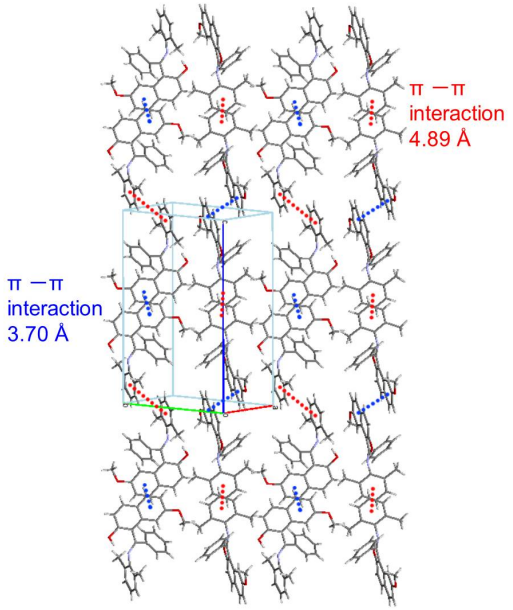

Figure 2. Molecular packing structure of title compound.

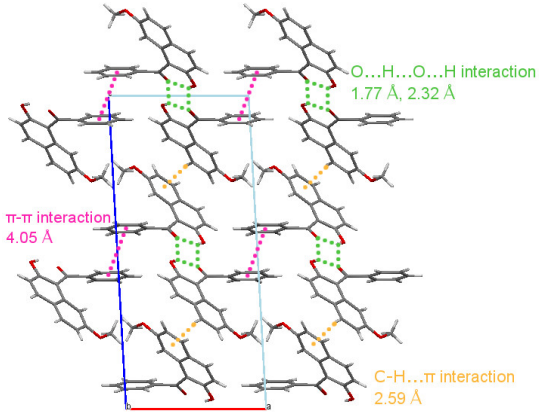

Figure 3. The crystal packing of 1-benzoyl-2-hydroxy-7-methoxy naphthalene, the precursor of the title compound.

The 2,7-dialkoxy-1,8-diaroylnaphthalene compounds generally demonstrate packing structure mainly formed through non-classical hydrogen bondings rather than π-π stacking interaction. This tendering is interpreted that non-coplanarly accumulated aromatic rings organization inhibits formation of satisfactorily effective π-π stacking, instead partial flexibility of bonding and dihedral angles around ketonic carbonyl group enables the sufficiently stabilized conformation by the aid of sum of various weak interactions such as non-classical hydrogen bondings. On the contrary, the near perpendicular alignment of the title compound, which have arylimino group in place of ketonic carbonyl one, brings about too stiff spatial alignment of single molecular structure to make a number of non-classical hydrogen bonding interactions through perturbation of relative positioning of aromatic rings. Whereas such an alignment exposes the π electrons of aromatic rings to two or three directions realizing formation of intermolecular π-π stacking. The precursor molecule also has hydroxy group at 2-position of naphthalene core, which acts a role of fixing for inner molecular motility through hydrogen bonding with oxygen atoms intramolecularly. However, the stabilization due to the sum of various non-classical hydrogen bondings is considered to overcome the fixation effect by 2-hydroxy group.

4. Conclusion

Conclusively, the distinct features in the accumulation crystal structures of the title triarylimine compound and the precursor diaryl ketone demonstrate that the spatial organization of the former is mainly determined π-π stacking interaction and for the latter the non-classical hydrogen bondings govern the spatial organization. Both of the compounds show non-coplanar accumulation of aromatic rings molecular structure. The title compound, 7-methoxy-1-{[(*E*)-2,6-dimethylphenylimino](phenyl)methyl}-2-naphthol, has molecular core of imino group which attaches three aromatic rings of *C*-1-naphthyl, *C*-phenyl, and *N*-phenyl stems of non-coplanar alignment of each aryl group to residual two aryl ones respectively, giving highly congested circumstance at the inner site of molecules. On the other hand, the precursor molecule, 1-benzoyl-2-hydroxy-7-methoxynaphthalene, has relatively large space compared to title compound, enabling conformational flexibility to some extent within restriction of maintaining non-coplanar organization. The molecules in crystal are stabilized by a number of non-covalent bonding interactions, mainly by non-classical hydrogen bondings. The achievement of stabilization contributed by a number of non-classical hydrogen bondings is considered to be due to the inner-molecular motility of single molecular structure. Contrarily, the congested inner-molecular situation of the title compound makes largely rigid molecular conformation, which affords at the same time exposure of three aromatic planes outside the molecular core. The single molecular organization permits π-π stacking interaction stabilization instead of formation of a number of weak interactions. Thus, the governing factors for the distinct feature of the single molecular and the accumulation structures of the title compound and the precursor compound are interpreted from the viewpoint of predominantly effective intermolecular interaction, a strong π-π stacking interaction or sum of weak non-classical hydrogen bondings, determined by the congestive conditions governing inner-molecular motility.

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Supplementary material

All crystallographic data for this paper are deposited in Cambridge Crystallographic Data Centre (CCDC 1524658). The data can be obtained free of charge at www.ccdc.cam.ac.uk or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 (0) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk.

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