SPATIAL ORGANIZATION OF BRIDGED *peri*-AROYLNAPHTHALENE COMPOUNDS HAVING 1,2- OR 1,3-BENZENEDIOXY-HINGE MOIETY IN SOLUTION

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Keywords: non-coplanarly aromatic ring accumulation, bridged structure, spatial organization in solution, specific magnetic field effect.

The bridged *peri*-aroylnaphthalene compounds having 1,3-benzendioxy-hinge units were newly synthesized and the spatial organization in solution was characterized in comparison with isomeric derivatives having 1,2-benzenedioxy-hinge unit and a non-bridged analogue. 1,2-Benzenedioxy and 1,3-benzendioxy-hinge units, which connect the edge carbon atoms of aroyl groups, afford the distinct difference in rotation ability of benzene ring of aroyl groups. The sharpness/broadness and the non-equivalency of ^{1}H NMR signals of aromatic protons demonstrate the highly congested and hinge-depending spatial organization of these bridged *peri*-aroylnaphthalene molecules. Furthermore, the significant magnetic field deviation of the signals in ^{1}H NMR spectra proves the presence of effective induced magnetic field especially for the middle proton at the 2-position of the 1,3-benzenedioxy unit.

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Introduction

Macrocyclic compounds having unique π-conjugated structures have been investigated as promising framework for organic optoelectronic devices.[1–5] To bring forth the excellent semiconductive properties, such as electrical conductivity, luminescence and photo-harvesting behavior, organic chemists and material scientists have attempted to design and synthesize the candidate molecules, e.g., incorporating phenylene motif by various bonding modes.[6] Along with these synthetic aspects, structural studies on spatial organization of aromatic ring accumulation compounds in solid state/solution are also being carried currently.[7–9] To grasp the spatial situation and the dynamic behavior of the aromatic rings in the aromatic ring accumulation structures, non-coplanarly accumulated aromatic ring compounds should be suitable model compounds. Because their weak π-conjugate system might reveal normally hidden structure-governing factors other than π…π stacking interactions. Our group has been studying on the spatial organization in crystal/solution of *peri*-aroylnaphthalene compounds, where two aroyl groups are situated at 1- and 8-positions of the adjacent inner carbons of the 2,7-dialkoxynaphthalene core.[10–14] In crystal, these compounds display a unique spatial organization feature of non-coplanar accumulation of aromatic rings. In most cases of *peri*-aroylnaphthalene compounds, the two aroyl groups are aligned in an opposite direction (i.e., *anti*-orientation).[15–19] Recently, we observed that, in crystalline state, the phenoxybenzoyl groups at 1- and 8-positions of the naphthalene ring in 2,7-dimethoxy-1,8-bis(4-phenoxybenzoyl)naphthalene (**3a**) are aligned in same direction i.e., in *syn*-orientation.[20] This finding prompted us to attempt to elucidate of the determining factors for orientations of two aroyl groups in *peri*-aroylnaphthalenes.[21] To achieve this aim, we have designed and synthesized bridged *peri*-aroylnaphthalene compounds having intramolecular connection between the terminal aromatic rings of the 1- and 8-benzoyl groups with catechol-hinge unit moiety (Figure 1, left).[22] The bridged compounds connected with suitable hinge at the edge carbons of the two aroyl groups plausibly have restricted conformation giving unique alignment of the molecular components including orientation and fixation of aroyl groups. Among the bridged homologous compounds with catechol ring-hinge, the analysis of the crystal structure of the catechol-bridged compounds (**1b**) was performed (Figure 2).

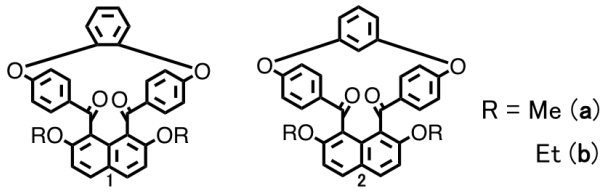


Figure 1. Bridged *peri*-aroylnaphthalene compounds.

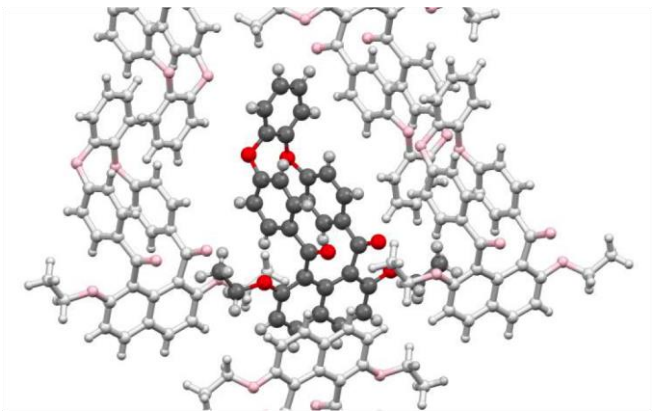


Figure 2. Crystal structure of bridged compound bearing catechol-hinge (**1b**).

Aromatic rings of the compound (**1b**) are accommodated non-coplanarly giving highly congested intramolecular circumstance. The plane of the catechol-hinge moiety almost parallels to the naphthalene ring. On the other hand, there are no strong interactions between aromatic rings within each molecule. The absence of effective intermolecular interaction means that conformation of the molecules of these compounds should be perturbed by addition of intramolecular/intermolecular interactions and possibly leads design of the analogues as synthetic unit. For application of these compounds as function-affording molecules in some practical material, understanding of the single molecular structure of the compound under non-crystalline state such as amorphous, liquid crystal, or solution is significantly important as well as that of the structural features in crystal. Based on such consideration, we have designed and synthesized another type of bridged compounds, which have resorcinol-hinge moiety at connecting 4,4'-position of aroyl groups instead of catechol unit for investigation of the spatial structure in solution (Figure 1, right).

In this paper, we report and discuss the characteristic features of molecular spatial organization of the bridged *peri*-aroylnaphthalene compounds in solution on the basis of comparison of their ^{1}H NMR spectra with those of non-bridged analogues.

Experimental

All reagents were of commercial quality and were used as received. Solvents were dried and purified using standard techniques.[23] 2,7-Dimethoxynaphthalene,[24] 2,7-diethoxy-naphthalene,[25] 2,7-diethoxy-1,8-bis(4-phenoxybenzoyl)-naphthalene (**3b**)[21] and the bridged *peri*-aroylnaphthalene compounds connected with 1,2-benzenedioxy moiety (**1**)[22] were prepared by reported methods.

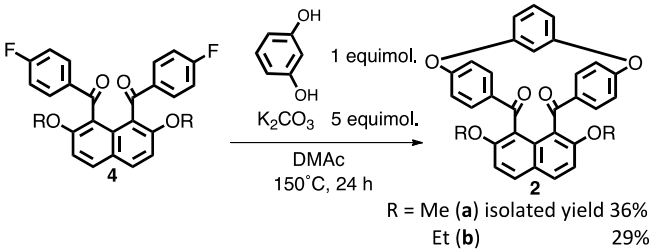
Measurements

^{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 (δ 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 $CDCl_3$ (δ 77.0). IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. High-resolution FAB mass spectra were recorded on a JEOL MStation (MS700) ion trap mass spectrometer in positive ion mode.

Synthesis of bridged *peri*-aroylnaphthalene (2)

To a solution of 1,8-bis(4-fluorobenzoyl)-2,7-dimethoxynaphthalene (0.3 mmol, 130.7 mg) in *N*,*N*-dimethylacetamide (DMAc, 7.5 mL), K_2CO_3 (1.5 mmol, 208.3 mg) and resorcinol (0.3 mmol, 34 mg) were added and the resulting solution was stirred at 423 K for 24 h. The reaction mixture was poured into aqueous 2 M HCl (75 mL) at room temperature (rt) resulting in formation of a pale yellow precipitate. The precipitate was collected by filtration and dried in vacuo giving crude product (143 mg; conversion 50 %). The crude material was purified by column chromatography (silica gel, $CHCl_3$: AcOEt = 3 : 1) and recrystallized from AcOEt to give the target compound (**2a**) (isolated yield 36 %; m.p. 453.7–455.4 K).

Compound (**2b**) was prepared in essentially the same way as that of compound (**2a**). The crude material was purified by column chromatography (silica gel, $CHCl_3$: AcOEt = 3 : 1) and recrystallized from AcOEt (isolated yield 29 %; m.p. 464.3–465.7 K). The synthetic procedure of the bridged compounds (**2**) is summarized as following scheme.



Scheme 1. Synthesis of the bridged compounds (**2**).

Spectral data

Compound (**2a**): ^{1}H NMR δ (300 MHz, $CDCl_3$): 8.14 (2H, dd, *J* = 8.7 Hz and 2.1 Hz), 8.00 (2H, d, *J* = 9.0 Hz), 7.26 (2H, d, *J* = 9.0 Hz), 7.23 (1H, t, *J* = 8.4 Hz), 7.18 (2H, dd, *J* = 8.7 Hz and 2.1 Hz), 6.94 (2H, dd, *J* = 8.7 Hz and 2.4 Hz), 6.74 (2H, dd, *J* = 8.4 Hz and 2.4 Hz), 6.62 (2H, dd, *J* = 8.7 Hz and 2.4 Hz), 4.01 (1H, t, *J* = 2.4 Hz), 3.76 (6H, s). ^{13}C NMR δ (75 MHz, $CDCl_3$): 56.79, 104.09, 109.17, 111.23, 121.05, 123.32, 124.22, 130.32, 130.42, 132.54, 133.28, 135.55, 156.66, 159.73, 161.76, 194.12 ppm. IR ν (KBr): 1677 (C=O), 1590, 1513, 1490 (Ar, naphthalene), 1497, 1609 (Ar, benzene), 1250 (C–O–C) cm^{-1}. HRMS (m/z): $[M+H]^+$ calcd. for $C_{32}H_{23}O_6$, 503.1489 found 503.1499.

Compound (**2b**): ^{1}H NMR δ (300 MHz, $CDCl_3$): 8.13 (2H, dd, *J* = 8.4 Hz and 2.4 Hz), 7.95 (2H, d, *J* = 8.7 Hz), 7.23 (1H, t, *J* = 8.4 Hz), 7.22 (2H, d, *J* = 8.7 Hz), 7.19 (2H, dd, *J* = 8.4 Hz and 2.4 Hz), 6.94 (2H, dd, *J* = 8.4 Hz and 2.4 Hz), 6.74 (2H, dd, *J* = 8.4 Hz and 2.4 Hz), 6.62 (2H, dd, *J* = 8.4 Hz and 2.4 Hz), 3.99–4.02 (1H, m), 3.94–4.16 (4H, m), 1.07 (6H, t, *J* = 7.2 Hz) ppm. ^{13}C NMR δ (75 MHz, $CDCl_3$): 14.66, 65.44, 104.10, 109.18, 112.50, 121.66, 123.16, 124.11, 130.20, 138.38, 132.33, 133.20, 135.73, 156.00, 159.60, 161.78, 194.09 ppm. IR ν (KBr): 1680 (C=O), 1590, 1512, 1490 (Ar, naphthalene), 1497, 1607 (Ar, benzene), 1250 (C–O–C) cm^{-1}. HRMS (m/z): $[M+H]^+$ calcd for $C_{34}H_{27}O_6$, 531.1808 found 531.1842.

Results and Discussion

The bridged compounds (**2**) were synthesized according to essentially the same synthetic method for bridged compounds (**1**), which was reported by us earlier.[22] In the previous paper, we reported the X-ray crystal structure of compound (**1b**) as displayed in Figure 2.[22] In this single crystal molecular structure there are no apparent effective intramolecular interactions either between aromatic rings of 1- and 8-benzoyl groups or between naphthalene ring and

catechol benzene ring. Furthermore, there are no strong intermolecular interactions also. These findings mean that the single molecular structure of compound (**1b**), in the crystal state is stabilized by weak van der Waals interactions. In other words, the stabilization factors of the single molecular structure originated from the spatial organization of the aromatic rings. In solution, where there are less intermolecular interactions, the structural features of the spatial organization might be more important. In view of this, we have investigated and compared the solution phase structure of bridged compounds (**1b**) and (**2b**) with that of non-bridged compound (**3b**) by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of bridged compounds (**1b**) and (**2b**) show four unique features, signal shapes of aromatic ring protons, non-equivalency of the symmetrically situated aromatic protons of the aroyl groups, deviation in characteristic chemical shifts of the signal assigned to the proton of the resorcinol, and the geminal protons in alkoxy groups at 2,7-positions of the naphthalene ring. First, in the aromatic region of ^{1}H NMR spectrum of non-bridged compound (**3b**), two signals attributed to the phenylene protons of the benzoyl groups appear at δ 7.68 and 6.88 ppm (Figure 3). While, in the ^{1}H NMR spectra of the bridged compounds, (**1b**) and (**2b**), four signals of the phenylene protons of the benzoyl groups appear with different chemical shifts for almost the same chemical structures with compound (**3b**), i.e., δ 7.80, 6.84, 6.54–6.74, and 6.20–6.40 ppm for compound (**1b**) (catechol-hinge derivative) and δ 8.14, 7.18, 6.94, and 6.62 ppm for compound (**2b**) (resorcinol-hinge derivative). The non-equivalency in aromatic H atoms and the significant deviation of chemical shifts are regarded as due to the unsymmetrical circumstance of magnetic field around macrocycle-forming accumulation of aromatic rings arising from restriction of the rotation of the benzoyl moieties of the compounds. Furthermore, the signal shapes of the aromatic protons are apparently different between catechol-hinge-bearing compound and resorcinol-hinge-bearing one. All four signals of the resorcinol-hinge-bearing compound are sharp, whereas two of four signals assigned as H(A3) and H(B3) protons in the catechol-hinge-bearing (**1b**) are broad.

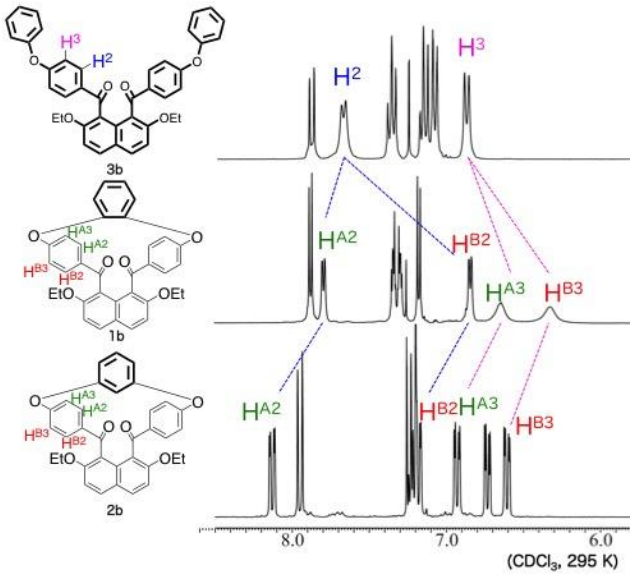


Figure 3. ^{1}H NMR study of compounds **3b**, **1b**, and **2b** in $CDCl_3$ (aromatic region).

The unsymmetrical signal shapes on the same aromatic ring in the catechol-hinge-bearing compound strongly indicate that magnetic influence by catechol moiety is unequal against the aromatic protons of the benzoyl group.

The spatial structure in solution of the resorcinol-hinge type compound (**2a**) is further investigated by the ^{1}H–^{1}H correlation spectroscopy (Figure 4). Correlation spectra between δ 3.25–4.75 ppm and δ 6.50–8.25 ppm regions show characteristic crossing feature. The signal of the H atom at 2-position of the resorcinol moiety drastically shifts from the general value of aromatic region to δ 4.00 ppm in the resorcinol-hinge-bearing compound (**2a**).

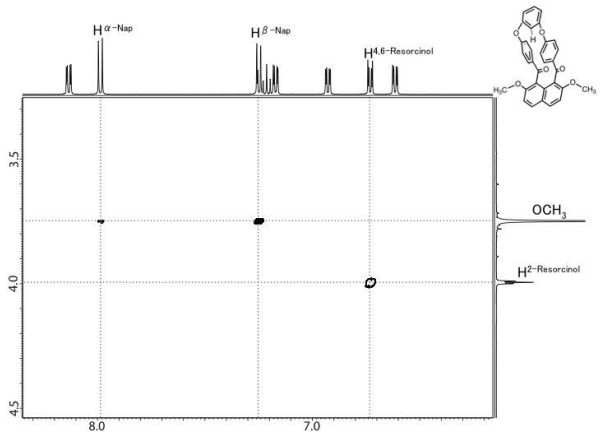


Figure 4. ^{1}H–^{1}H COSY spectrum of compound (**2a**), 500 MHz, at 293 K compound (**2a**) (*ca*. 0.02 mmol) was dissolved in $CDCl_3$ (0.5 mL).

This higher magnetic field deviation clearly displays the presence of significant and specific magnetic field effect. This is interpreted as caused by the rather fixed conformation, in which the H atom of resorcinol moiety is situated upon both of two benzene rings of the aroyl groups, i.e., being sandwiched among two aromatic π-systems resulting in doubly efficient shielding effect.

The signals of the methoxy groups at 2- and 7-positions of the naphthalene rings of bridged compounds (**1a**) and (**2a**) are observed as singlet in ordinary alkoxy region of the ^{1}H NMR spectra at about δ 3.5 to 4.5 ppm (Figure 5). The geminal protons of methyleneoxy group of ethoxy groups at 2- and 7-positions in non-bridged compound (**3b**) also show equivalency. On the other hand, in the ^{1}H NMR spectra of the bridged compounds (**1b**) and (**2b**), geminal non-equivalent signals appear. The ethoxy groups at 2- and 7-positions of the naphthalene rings are plausibly bulky enough to be restricted in rotation by the spatial hindrance of the fixed benzoyl groups. So the signals of $–CH_2O–$ are distinguished as geminally non-equivalent.

By connecting the two benzoyl groups of *peri*-aroylnaphthalene compounds, the rotation ability of the aromatic rings in the benzoyl moieties is reduced. On the other hand, the different shapes of signals between catechol-hinge-bearing bridged compound and resorcinol-hinge homologue reflect the difference in spatial arrangement and flexibility regulated by the substitution positions of the benzene ring connecting to the benzoyl groups to a greater or lesser degree (Figure 6).

We consider that the resorcinol-hinge moiety has relatively fixed conformation and the rotation of aromatic rings is strictly regulated in solution at room temperature. The spatial structure in solution may be closed to that in crystal state but the crystal structure has not been established so far. The rather flexible catechol-hinge-bearing molecule probably transforms the connected catechol moiety from standing up formation to lying down one repeatedly.

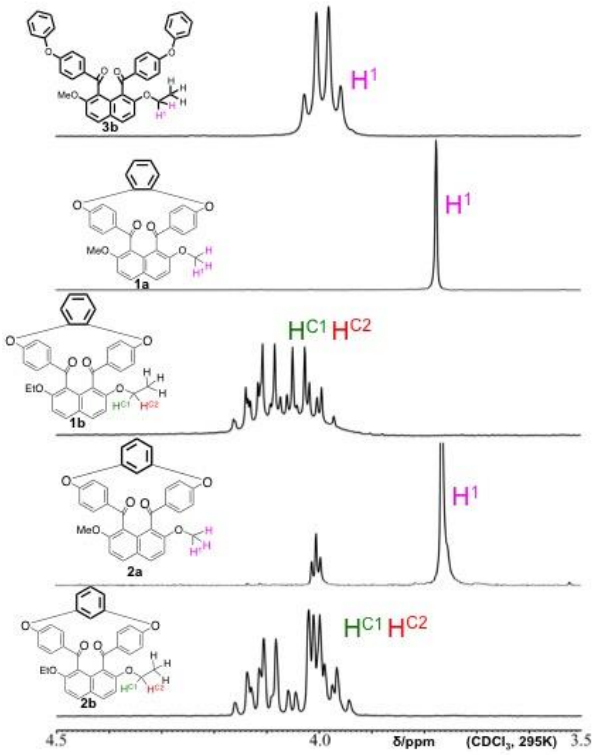


Figure 5. ^{1}H NMR study of compounds **3b**, **1a**, **1b**, **2a**, and **2b** in $CDCl_3$ (δ 3.5–4.5 ppm).

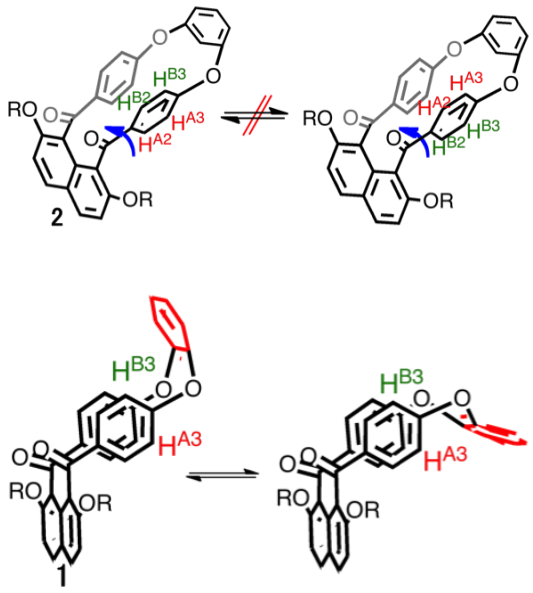


Figure 6. Plausible motions of bridged compounds **2** and **1** in solution.

Conclusion

We have studied the characteristic features of the spatial organization of bridged compounds (**1**) and (**2**) in solution by the aid of ^{1}H NMR spectroscopy. Signals of H atoms of the benzoyl groups appear with distinct shift values and different broadness. The observation is in accordance with the proposed structure in solution phase having restricted rotation for the benzene rings of benzoyl groups. There is a rather large differentiating feature between catechol-hinge compound and resorcinol-hinge one. A much higher magnetic field deviation of the signal of the proton at 2-position of resorcinol moiety in compound (**2**) indicates that the H atom is sandwiched and fixed between the π-systems of two benzoyl moieties. The bridged compound (**1**) also has a restricted rotation of the aromatic rings in the benzoyl moieties, whereas there is a free movement in the catechol-hinge-moiety. Furthermore, the rotation ability of the alkoxy groups in 2- and 7-positions in the naphthalene ring is proved to be reduced significantly. The molecular spatial organization of bridged *peri*-aroylnaphthalene compounds are shown to be highly congested. The tight arrangement of the aromatic rings in these compounds is crucial enough to be detected as deviation of chemical shift, shape of the signals of aromatic ring H atoms, and geminal non-equivalency in the adjacent alkoxy groups by ^{1}H NMR spectroscopy.

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