Aromatic Compounds with a 3a,6a-Dihydrofuro[2,3-*b*]furan Moiety. 2. Alkylation Products of Dihydroxynaphthalenes with 1,2-Dihydronaphtho[2,3-*b*]furan-1,2-diol and Their Structure Analyses†

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Received November 28, 1994®

The alkylation of 2,3-, 2,6-, and 2,7-dihydroxynaphthalenes (DHN) with 1,2-dihydronaphtho[2,1-*b*]furan-1,2-diol (**1**) in an acidic condition gave various products derived from 7a,14c-dihydronaphtho-[2,1-*b*]naphtho[1′,2′:4,5]furo[3,2-*d*]furan (**2a**). The products were characterized mainly by NMR spectroscopy with the help of the MNDO MO method. The reaction proceeds via two steps. The hydroxyl group-substituted **2a** first formed depending on the starting DHN. These **2a** derivatives reacted with another mole of **1** to give the corresponding products with two 3a,6a-dihydrofuro[2,3-*b*]furan moieties. The product from 2,7-DHN, however, formed in a poor yield, accompanying an unexpected **2a** derivative, due to a severe steric hindrance. Another method to prepare these compounds was examined using new precursors with four hydroxyl groups, corresponding to **1**.

Introduction

We have previously reported the base-catalyzed alkylation of 2-naphthol with glyoxal.[1] In this reaction, 1,2-dihydronaphtho[2,1-*b*]furan-1,2-diol (**1**) and 7a,14c-dihydronaphtho[2,1-*b*]naphtho[2′,1′:4,5]furo[3,2-*d*]furan (**2a**) were formed. In contrast to the method reported previously,[2-4] the procedure is characterized as a two-step reaction, where compound **1** is first formed in a basic medium and then reacts with 2-naphthol in the presence of an acid to give **2a**. Though several authors reported on the structure analyses of **2a**,[5,6] we have established the stereochemistry of **2a**, which has a *cis* configuration for the two hydrogens on the 7a and 14c carbons.[7]

Compound **1** was expected to react with 2,3-, 2,6-, and 2,7-dihydroxynaphthalenes (DHN) under an acidic condition to give a variety of aromatic compounds with 3a,-6a-dihydrofuro[2,3-*b*]furan (dihydrofurofuran) moieties. Some of them could also be obtained by another method via some tetrafunctional precursors.

There are many reports on the compounds with dihydro-, tetrahydro-, and hexahydrofuro[2,3-*b*]furan moieties and they are often found in the natural products (e.g., the extracts from leaves of various plants,[8a-c] aflatoxin,[9] and asteltoxin[10]). Maravigna synthesized thermally stable polymers directly from the reaction of diphenols with glyoxal.[3] The preparation methods starting from 2,3-dihydrofuran,[11] lithium di(3-furyl)cuprate,[8d,e] 2-nitrofuran derivatives,[12] hydroxyversicolorone,[13] and saccharides such as D-xylose[14] and D-glucose,[15] have been investigated. Cyclizations of dienone derivatives,[16] 1,5-bis(*tert*-butyldimethylsilyloxy)pentane-3-carbaldehyde,[17] and of unsaturated lactols,[18] and a photolytic ring expansion of cyclobutabenzofuranones[19] were also studied. However, the compounds we obtained have not been synthesized by these methods. Therefore, our alkylation method will afford another useful approach to construct the dihydrofurofuran system.

In this paper, we report the preparation of novel aromatic compounds with one or two dihydrofurofuran moieties starting from compound **1** and their structure analyses by NMR, MNDO method, etc.

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® Abstract published in *Advance ACS Abstracts,* July 1, 1995.

(1) Part I: Kito, T.; Yoshinaga, K.; Yamaye, M.; Mizobe, H. *J. Org. Chem.* **1991**, *56*, 3336.
(2) McGowan, J. C.; Anderson, J. M.; Walker, N. C. *Recl. Trav. Chim. Pays-Bas* **1964**, *83*, 597.
(3) Maravigna, P. J. *J. Polym. Sci. Part A: Polym. Chem.* **1988**, *26*, 2475.
(4) Taylor, D. A.; Ryan, G. R.; Allen, S. A. EP 595530 A1, 1994.
(5) Thyagarajan, B. S.; Balasubramanian, K. K.; Rao, R. B. *Can. J. Chem.* **1966**, *44*, 633.
(6) Coxworth, E. C. M. *Can. J. Chem.* **1967**, *45*, 1777.
(7) Fan, X.; Yamaye, M.; Kosugi, Y.; Okazaki, H.; Mizobe, H.; Yanai, T.; Kito, T. *J. Chem. Soc. Perkin Trans. 2* **1994**, 2001.
(8) (a) Kato, N.; Takahashi, M.; Shibayama, M.; Munakata, K. *Agric. Biol. Chem.* **1972**, *36*, 2579. (b) Kato, N.; Shibayama, M.; Munakata, K. *J. Chem. Soc. Perkin Trans. 1* **1973**, 712. (c) Hosozawa, S.; Kato, N.; Munakata, K. *Agric. Biol. Chem.* **1974**, *38*, 823. (d) Kojima, Y.; Kato, N. *Agric. Biol. Chem.* **1980**, *44*, 855. (e) Kojima, Y.; Kato, N. *Tetrahedron* **1981**, *37*, 2527.
(9) Schuda, P. F. *Top. Curr. Chem.* **1980**, 91.
(10) Kruger, G. J.; Steyn, P. S.; Vleggaar, R.; Rabie, C. J. *J. Chem. Soc., Chem. Commun.* **1979**, 441.
(11) Kraus, G. A.; Johnston, B. E.; Applegate, J. M. *J. Org. Chem.* **1991**, *56*, 5688.
(12) Makosza, M.; Niyazimbetov, M. *Synlett* **1992**, 417.
(13) Townsend, C. A.; Whittamore, P. R. O.; Brobst, S. W. *J. Chem. Soc., Chem. Commun.* **1988**, 726.
(14) Sharma, G. V. M.; Vepachedu, S. R. *Carbohydr. Res.* **1992**, *226*, 185.
(15) Tadano, K.; Yamada, H.; Idogaki, Y.; Ogawa, S.; Suami, T. *Tetrahedron Lett.* **1988**, *29*, 655.
(16) Yadav, J. S.; Rao, E. S.; Rao, V. S.; Choudary, B. M. *Tetrahedron Lett.* **1990**, *31*, 2491.
(17) Vader, J.; Sengers, H.; De Groot, A. *Tetrahedron* **1989**, *45*, 2131.
(18) Jalali, M.; Boussac, G.; Lallemand, J.-Y. *Tetrahedron Lett.* **1983**, *24*, 4307.
(19) Mittra, A.; Biswas, S.; Venkateswaran, R. V. *J. Org. Chem.* **1993**, *58*, 7913.

0022-3263/95/1960-5407$09.00/0

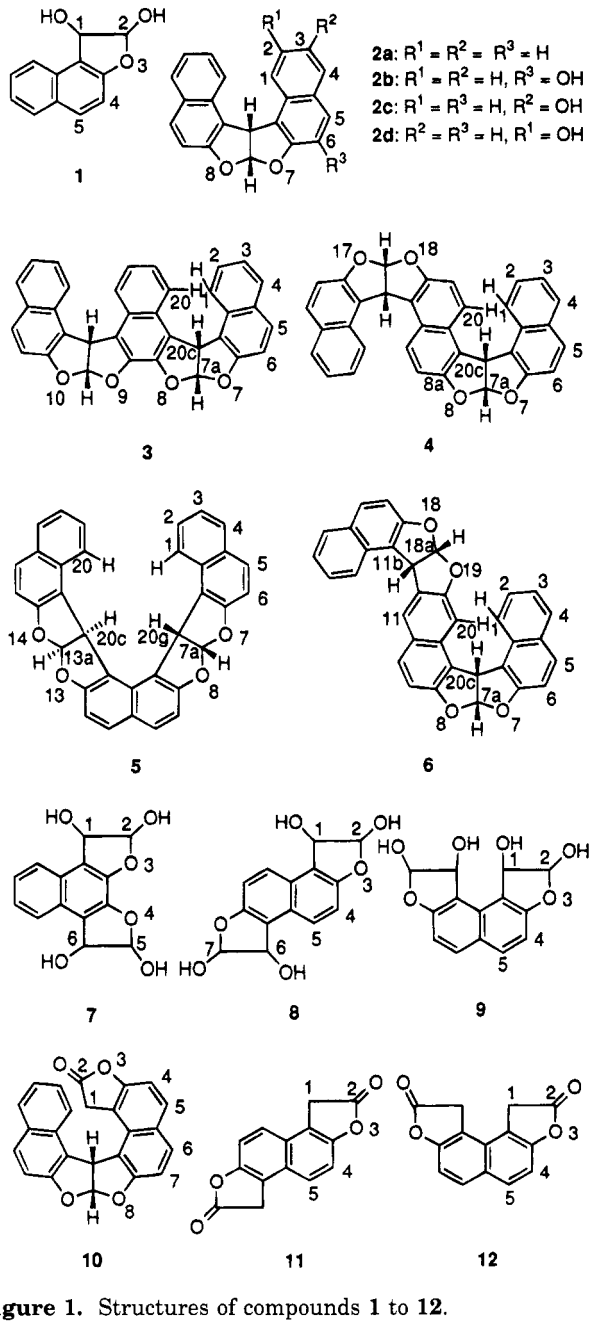

Figure 1. Structures of compounds **1** to **12**.

Results

Through the investigation of an acid-catalyzed alkylation of dihydroxynaphthalenes (DHN) with **1**, compounds **3** (from 2,3-DHN), **4** (from 2,6-DHN), **5** (from 2,7-DHN), **6** (from 2,7-DHN), and their related products **2b** (from 2,3-DHN), **2c** (from 2,6-DHN), and **2d** (from 2,7-DHN) were isolated, the starting materials being shown in parentheses. On the other hand, a base-catalyzed alkylation of DHN with glyoxal gave **7**, **8**, and **9**, all of which further reacted with 2-naphthol in an acidic medium to give **3**, **4**, and **10**, respectively. When 2-naphthol was absent, **8** and **9** were converted into their corresponding lactones, **11** and **12**, respectively. Figure 1 shows their structures which have been determined based on the following examinations (structures are shown as derivatives of **2a**).

The IR and ^{1}H NMR spectra showed that each of **2b**, **2c**, and **2d** has one hydroxyl group. The proton ratios of Ar*H*/*OH* (11:1) and Ar*H*/ArC*H*Ar (11:1) and the molecular weight of 326 measured by MS confirmed their structures shown in Figure 1.

Compounds **3**, **4**, and **6** were successfully obtained in a pure form, but **5** was formed only as a mixture with **6** (attempted separations failed because both **5** and **6** had poor solubilities). The proton ratio of Ar*H*/ArC*H*Ar (16:2) in the ^{1}H NMR spectra, the molecular weight of 492 for compounds **3**, **4**, **6**, and the mixture of **5** and **6** (**5**–**6** mixture) indicate that all of these compounds contain two dihydrofurofuran and three naphthalene moieties. No absorptions assigned to ν_{OH} were observed in the IR spectra of **3**, **4**, **6**, and the **5**–**6** mixture. Two doublets (5.79 and 5.82 ppm) appeared in the aliphatic region of the ^{1}H NMR spectrum of **6**, while only one doublet was observed for **3** at 5.90 ppm and for **4** at 5.94 ppm. In addition, two singlets (7.70 and 8.23 ppm) appeared in the spectrum of **6**, but none of the corresponding singlets were found in the spectra of **3** and **4**. These results indicate that **6** has an unsymmetrical structure and both of **3** and **4** possess symmetrical ones.

In the ^{1}H NMR spectrum of the **5**–**6** mixture, there were two singlets (7.70 and 8.23 ppm), doublets (5.79, 5.82, 6.26, 7.12, 7.14, 7.21, 7.26, 7.27, 7.45, 7.88, 7.92, 8.33, and 8.36 ppm), and two triplets (7.50 and 7.66 ppm), all of which were discriminated from one another. These signals were able to be assigned to those of **6** except signals at 6.26, 7.12, 7.45, 7.50, and 7.92 ppm. These five signals should be assigned to compound **5**, which was also formed from **2d**.

Compound **5** had only one type of methine proton (ArC*H*Ar, doublet at 6.26 ppm) with an integral ratio of 0.50H in the ^{1}H NMR spectrum of the **5**–**6** mixture, while the corresponding protons of **6** appeared at 5.79 ppm (0.75H) and 5.82 ppm (0.75H), indicating that the two methine protons in **5** (H_{20c} and H_{20g}) are equivalent under the same chemical environment. This suggests that **5** has a symmetrical structure shown in Figure 1. Based on the integral ratio of the methine protons, the molar ratio of **5**/**6** in the mixture was 0.25/0.75. The other proton signals (7.12, 7.45, 7.50, and 7.92 ppm) of **5** also had the same integral ratio of 0.50H.

In the ^{13}C NMR spectrum of the **5**–**6** mixture, there were three signals at 48.4, 48.5, and 51.2 ppm for two ArCHAr carbon atoms and six signals at 154.8, 155.4, 155.7, 156.3, 157.0, and 157.9 ppm for the aromatic carbons adjacent to the oxygen atom. These signals can be attributed to those of **6** except those at 51.2, 155.4, and 157.9 ppm; these three signals also confirm the symmetrical nature of **5**. In addition, the molecular weight (492) and elemental analysis support the structure.

Compounds **7**–**9** gave the same molecular weight and their IR spectra showed a ν_{OH} (broad and strong) at 3300–3500 cm^{-1}. The proton ratio of O*H*/Ar*H*/ArC*H* + ArOC*H* (4:4:4) also supports the structures of **7**–**9** given in Figure 1.

TG analysis suggests that each of compounds **7**–**9** has several moles of combined water. The calculated weight losses are 11.54, 6.12, and 3.16% when these compounds contain $2H_2O$, H_2O, and $^1/_2H_2O$, respectively. The observed weight losses (determined below 140 °C) were 3.20 (for **7**), 11.63 (for **8**), and 3.50% (for **9**). Thus, both **7** and **9** carry $^1/_2$ mol of combined water, while **8** contains 2 mol of water. Therefore, these compounds should be written as **7**·$^1/_2H_2O$ (mw 285), **8**·$2H_2O$ (mw 312), and **9**·$^1/_2H_2O$ (mw 285). The elemental analyses also support these results,

Table 1. Reaction Conditions and Products (Summary)

exp no.	reaction[a] (mmol)	sovlent[b] (mL)	cat.[c] (mL)	conditions[d] °C/h	products (yield, %)
1	**1** (10.0) + 2,3-DHN (10.0)	Ace (20)	MSA (3)	rt/6.5	**2b** (12) + **3** (36)
2	**1** (20.0) + 2,3-DHN (10.0)	DME (20)	SA (3)	rt/24	**2b** (7.3) + **3** (58)
3	**7** (2.7) + 2-Naph (4.2)	DME (20)	MSA (4)	rt/24	**3** (11)
4	**1** (16.0) + 2,6-DHN (16.0)	Ace (40)	MSA (4)	rt/18	**2c** (50) + **4** (22)
5	**1** (6.8) + 2,6-DHN (3.4)	DME (30)	MSA (5)	rt/3	**4** (98)
6	**1** (6.8) + 2,6-DHN (3.4)	DME (30)	SA (3)	rt/3	**4** (78)
7	**8** (1.3) + 2-Naph (13.9)	DME (20)	SA (3)	rt/6	**4** (50)
8	**1** (7.0) + 2,7-DHN (3.5)	DME (20)	MSA (3)	rt/24	**6** (21)
9	**1** (132.0) + 2,7-DHN (68.0)	Ace (50)	MSA (5)	60/12	**2d** (72) + **5** + **6** (mixture, 5.4)
10	Gly (345.0) + 2,3-DHN (31.3)	water (50)	KOH (5)	20/3	**7** (56)
11	Gly (75.2) + 2,6-DHN (6.3)	water (20)	KOH (2)	20/5	**8** (99)
12	Gly (345.0) + 2,7-DHN (31.3)	water (50)	KOH (5)	20/3	**9** (60)
13	**9** (3.4) + **2**-Naph (8.3)	DME (20)	MSA (4)	rt/24	**10** (21)
14	**8** (1.8)	DME (15)	MSA (4)	40/24	**11** (33)
15	**9** (3.8)	DME (20)	MSA (4)	45/24	**12** (75)

[a] 2-Naph: 2-naphthol. Gly: glyoxal (40%, aq). [b] Ace: acetone. DME: 1,2-dimethoxyethane. [c] SA: sulfuric acid (98%). MSA: methanesulfonic acid. KOH: 1 N solution. [d] rt: room temperature.

while all of their MS spectra showed only 276 for the parent molecular ion in the anhydrous state.

The weight losses of 12.50 (for **7**), 11.50 (for **8**), and 12.45% (for **9**) at 140−230 °C can be attributed to the lactone formation by the elimination of 2 mol of water from the parent compounds. Upon heat treatment of **7**−**9** (heating at a rate of 25 °C/min to 220 °C), a strong lactone $\nu_{C=O}$ absorption appeared at 1800 cm^{-1} in the IR spectra, whereas the ν_{OH} absorption at 3000−3500 cm^{-1} disappeared.

Compound **10** (prepared from **9** and 2-naphthol) gave a molecular weight of 366 and had a strong absorption at 1790 cm^{-1} and no appreciable absorptions above 3000 cm^{-1} in the IR spectrum. The proton ratios of Ar*H*/C*H*$_2$ (10/2) and Ar*H*/ArC*H*Ar (10/1) in the ^{1}H NMR spectrum and the presence of one methylene (34.9), methine (49.0), and carbonyl carbon (174.3 ppm) in the ^{13}C NMR spectrum supports the structure of **10** shown in Figure 1.

We previously reported that the elimination of water from compound **1** led to the corresponding lactone, naphtho[2,1-*b*]furan-2(1*H*)-one, when **1** was treated with an acid.[1] Similar treatments of **8** and **9** at 40−50 °C gave the corresponding lactones **11** and **12**, respectively. The proton ratio of Ar*H*/C*H*$_2$ (1/1) in the ^{1}H NMR spectra, a strong absorption at 1790 cm^{-1} ($\nu_{C=O}$ of lactone) in the IR spectra, and a molecular weight of 240 all confirmed the structures given for **11** and **12** in Figure 1. Formation of **11** and **12** from **8** and **9**, respectively, also supports the structures given for **8** and **9** in Figure 1.

Discussion

As reported previously, the alkylation of 2-naphthol with glyoxal in the presence of potassium hydroxide gave **1** in a good yield, which, upon addition of an acid, further reacted with another mole of 2-naphthol to form **2a**.[7]

This two-step procedure was applied to the alkylation of DHN with **1**. The reaction of 2,3-, 2,6-, or 2,7-DHN with **1** gave mixtures of (**2b** + **3**), (**2c** + **4**), and (**2d** + **5**+**6**), respectively.

The yield of these compounds largely depended on the molar ratio of DHN/**1** (see Table 1). For example, the yield ratios (%/%) of **3**/**2b**, **4**/**2c**, and **5**+**6**/**2d** were 58/7.3, 98/0, and 5.4/72, respectively, when a molar ratio of DHN (2,3-, 2.6-, or 2.7-DHN)/**1** was 1/2. With the molar ratio of 1/1, the yield ratios for the former two changed into 36/12 and 22/50, respectively. These results can explain the following reaction scheme.

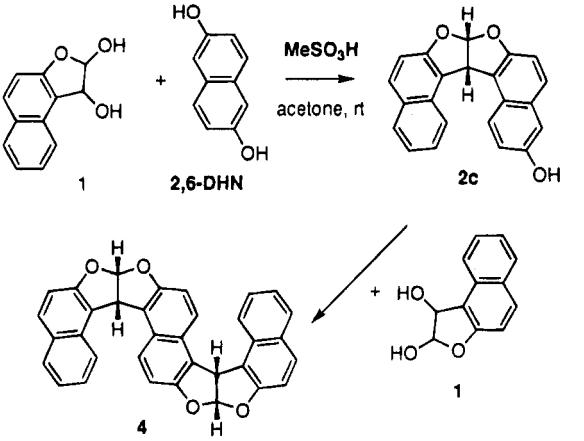

Figure 2. Preparation of **4** from **1** and 2,6-DHN.

The reaction of DHN with **1** proceeds via two steps. In the first step, 2,3-, 2,6-, and 2,7-DHN react with one molecule of **1** to form **2b**, **2c**, and **2d**, respectively. In the second step, **2b** and **2c** readily react with another molecule of **1** to give **3** and **4**, respectively. Formation of **4** from 2,6-DHN and **1** is exemplified in Figure 2. However, the reaction of **2d** with **1** gives **5** only in a poor yield, accompanying the formation of an unexpected product **6**. The yield ratio (%/%) of **5**/**6** was 1.3/4.0 when the reaction was carried out at 60 °C, but 0/21 at room temperature. The reactivity of the α-position (C_1 in **2d**) of the naphthalene ring is generally greater than that of the β-one (C_3) in an electrophilic reaction. However, large steric hindrance must be overcome in the pathway from **2d** to **5**. On the other hand, there will be no appreciable hindrance present during the formation of **6** when reaction takes place at the C_3 position in **2d**. Therefore, **6** can be formed more easily than **5** in spite of the lower reactivity of the β-position (C_3) of **2d**.

On the basis of the stereochemistry of compound **2a** reported previously,[7] the two hydrogens (one methine and one acetal) on the C_{3a} and C_{6a} atoms of the dihydrofurofuran moieties should be *cis* to each other. Because all of compounds **3**−**6** have two dihydrofurofuran moieties each, there are two possible configurations for the structures of **3**−**6** with respect to the two pairs of hydrogens on the two dihydrofurofuran moieties. One is *syn* (**3**$_{syn}$, **4**$_{syn}$, **5**$_{syn}$, and **6**$_{syn}$), and the other *anti* (**3**$_{anti}$, **4**$_{anti}$, **5**$_{anti}$, and **6**$_{anti}$). Their heats of formation (H_f) and geometrical parameters were calculated by the MNDO method and are summarized in Tables 2−4. The ener-

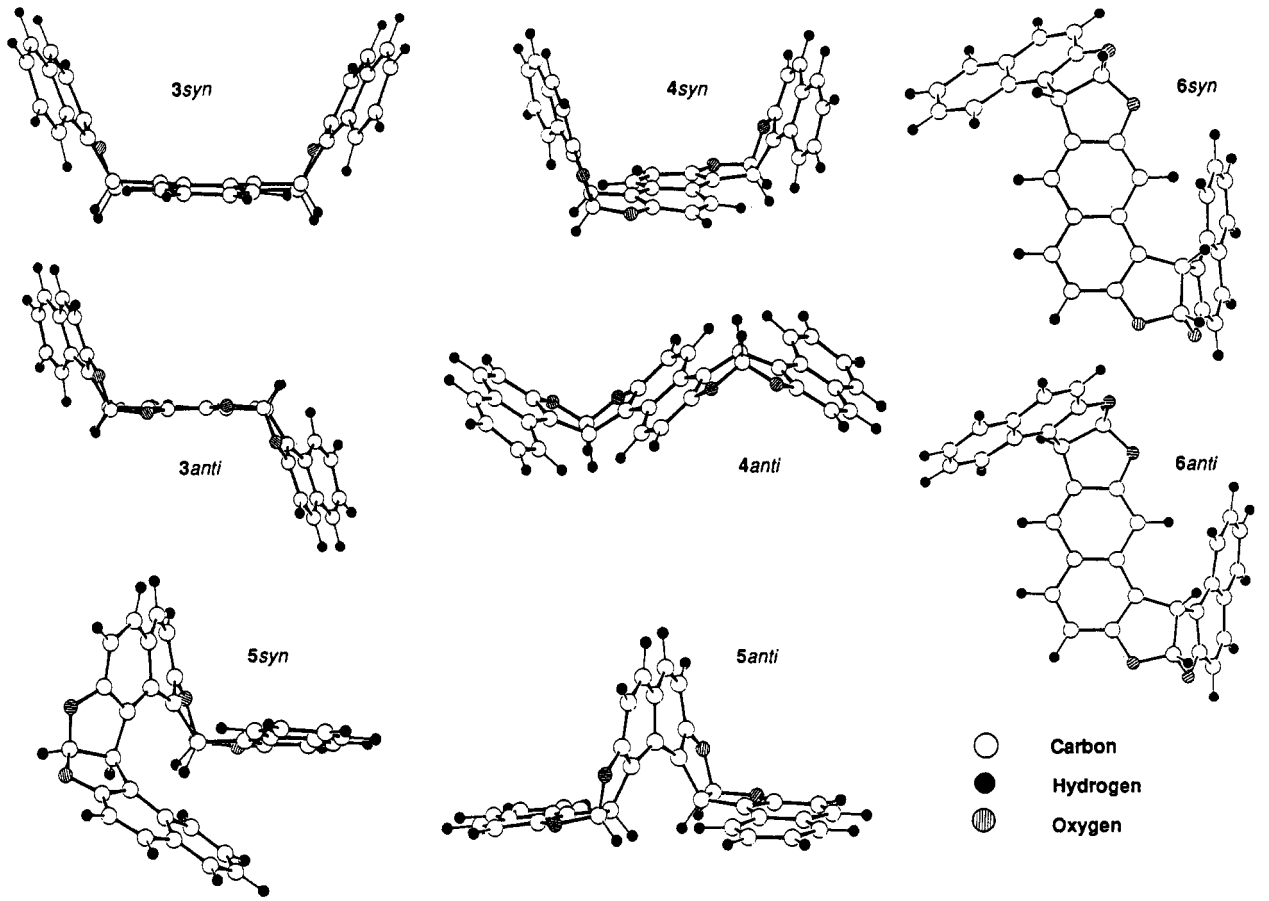

Figure 3. Energetically optimized structures.

Table 2. Heat of Formation (H_f) for Compounds 3–6 by MNDO Method

compound	H_f (kcal/mol) syn	anti
3	0.46	−0.52
4	−2.48	−2.17
5	22.61	2.26
6	−10.66	−10.01

Table 3. Geometrical Parameters of 3 and 4 by MNDO Method[a,b]

compound **3**			compound **4**		
bond angle (deg)	syn	anti	bond angle (deg)	syn	anti
$O_7-C_{6a}-C_{20d}$	114.10	113.98	$O_7-C_{6a}-C_{20d}$	114.10	114.06
$C_{6a}-C_{20d}-C_{20c}$	107.81	107.81	$C_{6a}-C_{20d}-C_{20c}$	107.71	107.80
$C_{20d}-C_{20c}-C_{7a}$	100.37	100.55	$C_{20d}-C_{20c}-C_{7a}$	100.45	100.54
$C_{20c}-C_{7a}-O_7$	107.90	107.60	$C_{20c}-C_{7a}-O_7$	107.55	107.77
$C_{7a}-O_7-C_{6a}$	109.20	109.34	$C_{7a}-O_7-C_{6a}$	109.29	109.21
$O_7-C_{7a}-O_8$	106.34	106.55	$O_7-C_{7a}-O_8$	106.62	106.49
$C_{20b}-C_{20c}-C_{20d}$	119.23	118.48	$C_{20b}-C_{20c}-C_{20d}$	118.85	118.54
distance (Å)	syn	anti	distance (Å)	syn	anti
H_1-H_{20}	1.993	2.085	H_1-H_{20}	2.068	2.055
H_1-H_{20c}	2.673	2.662	H_1-H_{20c}	2.645	2.676
$H_{20}-H_{20c}$	2.676	2.705	$H_{20}-H_{20c}$	2.720	2.647
$H_{7a}-H_{20c}$	2.483	2.491	$H_{7a}-H_{20c}$	2.492	2.490

[a] Bond angles for furan ring containing O_8 agree within 1° from the corresponding ones for the other ring containing O_7. [b] Geometrical parameters are shown for the half of the structure of **3** and **4**, due to symmetry about the central naphthalene ring.

getically optimized molecular structures were depicted in Figure 3 using ORTEP routine.[20]

The H_f differences between $\mathbf{3}_{syn}$ and $\mathbf{3}_{anti}$ (0.98 kcal/mol) as well as $\mathbf{4}_{syn}$ and $\mathbf{4}_{anti}$ (0.31 kcal/mol) calculated from H_f values in Table 2 are small. The energetically optimized structures given in Figure 3 show that $\mathbf{3}_{syn}$, $\mathbf{3}_{anti}$, $\mathbf{4}_{syn}$, and $\mathbf{4}_{anti}$ all have nearly symmetrical structures. As for the geometrical parameters in Table 3, the corresponding bond angles for the *syn* and *anti* isomers are virtually equal to each other and suggest the symmetrical structure for **3** and **4**, too. These results, therefore, indicate that both forms of each pair, $\mathbf{3}_{syn}$ and $\mathbf{3}_{anti}$, or $\mathbf{4}_{syn}$ and $\mathbf{4}_{anti}$, may exist in nearly the same probability.

Seventeen signals were found in the ^{13}C NMR spectra of the mixture of $\mathbf{3}_{syn}$ and $\mathbf{3}_{anti}$, and of $\mathbf{4}_{syn}$ and $\mathbf{4}_{anti}$; both of **3** and **4** consist of 34 carbons in the molecular framework. The methine protons (ArC*H*Ar) showed only one doublet at 5.90 ppm for **3** and 5.94 ppm for **4**, both with the integral ratio of 2H in the ^1H NMR spectra. The numbers of signals in the ^{13}C and ^1H NMR spectra indicate that both **3** and **4** have a symmetrical structure, a conclusion being compatible with the results calculated by the MNDO method. Because the protons and carbons in $\mathbf{3}_{syn}$ and $\mathbf{3}_{anti}$ have almost the same chemical environment, we can expect that they will give similar NMR spectra. In fact, $\mathbf{3}_{syn}$ cannot be distinguished from $\mathbf{3}_{anti}$ by ^1H and ^{13}C NMR spectroscopy. This discussion also is the case for $\mathbf{4}_{syn}$ and $\mathbf{4}_{anti}$.

In comparison between the H_f's of **6** and those of **5** (see Table 2), **6** has a lower H_f value so that **6** will be a more stable compound than **5** and should be the major product. This inference is in agreement with the experimental results. Both $\mathbf{6}_{syn}$ and $\mathbf{6}_{anti}$ isomers may exist in nearly the same ratio, since the H_f difference is small (0.65 kcal/

(20) Johnson, C. K. *ORTEP-II; A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*, Oak Ridge National Laboratory, TN, 1976.

Table 4. Geometrical Parameters of 5 and 6 by MNDO Method

compound 5						compound 6					
bond angle (deg)	syn	anti	bond angle (deg)	syn	anti	bond angle (deg)	syn	anti	bond angle (deg)	syn	anti
$O_7-C_{6a}-C_{20h}$	114.10	114.26	$O_8-C_{8a}-C_{20f}$	113.93	113.92	$O_7-C_{6a}-C_{20d}$	114.25	114.18	$O_8-C_{8a}-C_{20b}$	113.79	113.98
$C_{6a}-C_{20h}-C_{20g}$	107.68	107.73	$C_{8a}-C_{20f}-C_{20g}$	105.63	106.95	$C_{6a}-C_{20d}-C_{20c}$	107.68	107.82	$C_{8a}-C_{20b}-C_{20c}$	107.85	107.68
$C_{20h}-C_{20g}-C_{7a}$	100.10	100.37	$C_{20f}-C_{20g}-C_{7a}$	100.98	100.48	$C_{20d}-C_{20c}-C_{7a}$	100.82	100.46	$C_{20b}-C_{20c}-C_{7a}$	100.47	100.43
$C_{20g}-C_{7a}-O_7$	108.05	108.16	$C_{20g}-C_{7a}-O_8$	106.30	106.94	$C_{20c}-C_{7a}-O_7$	107.88	108.11	$C_{20c}-C_{7a}-O_8$	107.55	107.70
$C_{7a}-O_7-C_{6a}$	108.93	109.11	$C_{7a}-O_8-C_{8a}$	108.96	109.13	$C_{7a}-O_7-C_{6a}$	109.28	109.15	$C_{7a}-O_8-C_{8a}$	109.30	109.29
$O_{13}-C_{12a}-C_{20d}$	114.73	113.94	$O_{14}-C_{14a}-C_{20b}$	113.92	114.26	$O_{18}-C_{17a}-C_{11c}$	114.09	114.12	$O_{19}-C_{19a}-C_{11a}$	112.39	112.66
$C_{12a}-C_{20d}-C_{20c}$	105.85	106.98	$C_{14a}-C_{20b}-C_{20c}$	108.34	107.74	$C_{17a}-C_{11c}-C_{11b}$	107.68	107.83	$C_{19a}-C_{11a}-C_{11b}$	107.97	107.70
$C_{20d}-C_{20c}-C_{13a}$	99.45	100.48	$C_{20b}-C_{20c}-C_{13a}$	99.74	100.38	$C_{11c}-C_{11b}-C_{18a}$	101.28	101.03	$C_{11a}-C_{11b}-C_{18a}$	101.17	101.19
$C_{20c}-C_{13a}-O_{13}$	106.94	106.97	$C_{20c}-C_{13a}-O_{14}$	106.98	107.35	$C_{11b}-C_{18a}-O_{18}$	107.44	107.66	$C_{11b}-C_{18a}-O_{19}$	108.24	108.12
$C_{13a}-O_{13}-C_{12a}$	108.88	109.11	$C_{13a}-O_{14}-C_{14a}$	108.40	109.08	$C_{18a}-O_{18}-C_{17a}$	109.38	109.31	$C_{18a}-O_{19}-C_{19a}$	110.10	109.94
$O_7-C_{7a}-O_8$	106.91	107.08	$O_{13}-C_{13a}-O_{14}$	104.39	107.04	$O_7-C_{7a}-O_8$	106.96	106.22	$O_{18}-C_{18a}-O_{19}$	107.38	107.18
$C_{20f}-C_{20g}-C_{20h}$	117.63	119.84	$C_{20b}-C_{20c}-C_{20d}$	124.52	119.95	$C_{20b}-C_{20c}-C_{20d}$	118.96	119.28	$C_{11a}-C_{11b}-C_{11c}$	117.95	117.83
distance (Å)	syn	anti	distance (Å)	syn	anti	distance (Å)	syn	anti	distance (Å)	syn	anti
H_1-H_{20}	3.260	4.643	$H_{20}-H_{20c}$	2.722	2.993	H_1-H_{20}	2.115	1.987	$H_{11}-H_{11b}$	3.071	3.081
H_1-H_{20g}	3.118	2.995	$H_{20}-H_{20g}$	1.854	2.445	H_1-H_{20c}	2.845	2.760	$H_{11}-H_{12}$	2.451	2.437
H_1-H_{20c}	4.110	2.442	$H_{20c}-H_{20g}$	2.755	2.332	$H_{20}-H_{20c}$	2.607	2.656	$H_{11b}-H_{12}$	2.761	2.789

mol). As shown in Figure 3 and Table 4, both of $\mathbf{6}_{syn}$ and $\mathbf{6}_{anti}$ have unsymmetrical structures, and their corresponding bond angles are almost the same. The bond-angle deviations in the dihydrofurofuran ring from the standard value (109.5°) for $\mathbf{6}_{syn}$ and $\mathbf{6}_{anti}$ are smaller than those for $\mathbf{5}_{syn}$ and $\mathbf{5}_{anti}$. For example, the bond angles of $C_{11a}-C_{11b}-C_{18a}$ for $\mathbf{6}_{syn}$ and $\mathbf{6}_{anti}$ are 101.17 and 101.19°, respectively, while the corresponding angles of $C_{20d}-C_{20c}-C_{13a}$ for $\mathbf{5}_{syn}$ and $\mathbf{5}_{anti}$ are 99.45 and 100.48°, respectively. Therefore, $\mathbf{6}_{syn}$ and $\mathbf{6}_{anti}$ are more stable than $\mathbf{5}_{syn}$ and $\mathbf{5}_{anti}$. However, the separation of $\mathbf{6}_{syn}$ and $\mathbf{6}_{anti}$ was unsuccessful and no difference between the structures of both isomers was noted in the NMR spectrum of **6** ($\mathbf{6}_{syn}$ + $\mathbf{6}_{anti}$).

As for compound **5**, $\mathbf{5}_{anti}$ will be more stable than $\mathbf{5}_{syn}$, because there is a great difference in H_f (ΔH_f = 20.35 kcal/mol). The structures given for $\mathbf{5}_{syn}$ and $\mathbf{5}_{anti}$ in Figure 3 tell us that the central naphthalene ring of $\mathbf{5}_{syn}$ is forced to twist in order to diminish overlapping of the two naphthalene rings at both ends, but the corresponding two naphthalene rings of $\mathbf{5}_{anti}$ direct to the opposite side to each other as shown in Figure 3. The geometrical parameters in Tables 3 and 4 show that the angle distortions in $\mathbf{5}_{syn}$ are the greatest. For example, the bond angles of $C_{20b}-C_{20c}-C_{20d}$ for the *syn* and *anti* forms were 119.23 and 118.48° for compound **3**, 118.85 and 118.54° for **4**, 124.52 and 119.95° for **5**, and 118.96 and 119.28° for **6**. Of these, the bond angle for $\mathbf{5}_{syn}$ showed the largest deviation from the standard one (109.5°). A similar trend can be seen for the other corresponding angles as shown in Table 3 and 4.

Therefore, the reason why $\mathbf{5}_{syn}$ has the highest H_f value can be attributed to the angle distortion and overlapping of the two naphthalene rings. In practice, we found a great difficulty in constructing the framework of $\mathbf{5}_{syn}$ by STS molecular model. As for $\mathbf{5}_{anti}$, on the other hand, there is no appreciable crowding. The calculated interatomic H_1-H_{20c} distance, the shortest one between hydrogens, in $\mathbf{5}_{anti}$ was 2.442 Å, a value twice larger than the van der Waals radius for the hydrogen atom (1.2 Å).[21] Nevertheless formation of $\mathbf{5}_{anti}$ was more difficult than that of **6**. One of the major reasons for this may be that there is a severe steric hindrance in the transition state leading to $\mathbf{5}_{anti}$.

As shown in Figure 3 and Table 4, $\mathbf{5}_{syn}$ has an unsymmetrical structure, but $\mathbf{5}_{anti}$ has a symmetrical one. According to the ^1H and ^{13}C NMR spectra of the **5**–**6** mixture, the signals excluding those for **6** became symmetrical (see the Results section). Therefore, both of NMR spectroscopy and MNDO calculation suggest that $\mathbf{5}_{anti}$ is the only isomer for compound **5** existing in the **5**–**6** mixture.

Another route (method b) to compounds **3**, **4**, and **5** from **7**, **8**, and **9**, respectively, has been investigated. Compounds **7** and **8** reacted with 2-naphthol in the presence of methanesulfonic acid to give **3** and **4**, respectively, but their yields were lower than those by method a. On the other hand, the reaction of **9** with 2-naphthol gave only **10**; the expected product **5** was not found (this reaction route can not give **6**), indicating that a large steric hindrance may arise between the naphthalene rings in the pathway from **9** to **5**. Although method b was inferior to method a for preparation of **3** and **4**, the former method would be promising for obtaining novel aromatic polymers with dihydrofurofuran moieties from condensation of **7** or **8** with DHN or related compounds containing two hydroxyl groups.

In summary, a practical and convenient preparation of unique aromatic compounds carrying the dihydrofurofuran ring system has been accomplished. The key to this successful preparation is the use of readily available compound **1** as the starting material.

Experimental Section

General. Proton and ^{13}C NMR spectra were recorded on a Bruker AC-250 (250 MHz) and JEOL GX-400 (400 MHz). DMSO-d_6 was used as a solvent unless otherwise mentioned. Chemical shifts are expressed in ppm, and the J values are in hertz. MS spectra were obtained on a JEOL JMS-DX300 at 70 eV, IR spectra on a Shimadzu IR-408 or JEOL JIR-5500 spectrometer, and UV spectra (λ_{max} in nm (log ϵ)) on a JASCO V-520-SR spectrometer. Thermal analysis was given by means of a Shimadzu TGA-50 (heating rate 25 °C/min) and DSC-50 (heating rate 5 °C/min). Melting points were determined by DSC. The structures of compounds **1** to **12** are shown in Figure 1.

Molecular Model. The STS molecular model, a space-filling model (Stuart model) manufactured by Maruzen, Tokyo, Japan, was used.

MO Calculation. Geometrical parameters and heats of formation (H_f) for compounds **3**–**6** were obtained from energetically optimized calculation by the semiempirical MNDO MO method[22] using MOPAC (ver. 6.01 and ver. 7.00),[23,24] and listed in Tables 2–4.

(21) *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1985; Section 3 (Table 3–10).

(22) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

1,2-Dihydronaphtho[2,1-*b*]furan-1,2-diol (1). For synthesis and analyses (except UV data) for **1**, see ref 1. UV (water) 232 (3.98), 268 (3.62), 278 (3.70), 289 (3.60), 323 (3.40), 335 (3.45).

7a,14c-Dihydronaphtho[2,1-*b*]naphtho[1′,2′:4,5]furo-[3,2-*d*]furan (2a). For synthesis and analyses (except UV data) for **2a**, see ref 7. UV (acetonitrile) 240 (4.23), 281 (3.89), 292 (3.85), 336 (3.77).

Preparation of Aromatic Compounds 2b, 2c, 2d, 3, 4, 5, and 6. A typical example (**2c** and **4**) is described. Methanesulfonic acid (4 mL) was added dropwise to a solution of **1**·H_2O (1.60 mol) and 2,6-DHN (1.60 mol) in acetone. After stirring for 18 h at room temperature, precipitates formed were collected by filtration and then washed successively with acetone, water, and hexane and dried to give **4** in 22% yield. Evaporation of the solvent under reduced pressure from the filtrate left the residue, which was washed with ether and water and then recrystallized from benzene to give **2c** in 50% yield. The reaction conditions and yields of products obtained in this study are shown in Table 1.

7a,14c-Dihydronaphtho[2,1-*b*]naphtho[1′,2′:4,5]furo-[3,2-*d*]furan-6-ol (2b) (exp. no. 1 and 2). The compound was prepared from 2,3-DHN: mp 163 °C (from benzene); IR (KBr, cm^{-1}) 3440 (ν_{OH}), 1627, 1592, 1527, 1465, 1276, 1243, 1213, 1062, 809, 738 (characteristic of 1,2-disubstituted naphthalene); UV (acetonitrile) 239 (4.28), 285 (3.86), 293 (3.89), 328 (3.66); ^1H NMR (250 MHz) δ 5.89 (d, 1H, ArC*H*Ar), 7.1 (s, 1H), 7.3 (m, 5H), 7.5 (t, 1H), 7.7 (d, 1H), 7.9 (t, 2H), 8.26 (d, 1H), 8.33 (d, 1H), 10.1 (s, 1H, O*H*). A signal at 10.1 ppm disappeared upon addition of D_2O; ^{13}C NMR (62.9 MHz, Only signals separated clearly were shown.) δ 49.1 (d, Ar*C*HAr), 111.6, 114.8, 118.7, 120.3, 123.1, 123.3, 123.6, 124.3, 126.5, 126.9, 128.8, 129.6, 129.9, 130.3, 130.9, 142.8 (s), 147.2 (s), 155.7 (s) (The last three signals are assigned to the aromatic *C*'s adjacent to the O atom. The signal for ArO*C*HOAr is in the aromatic region); MS *m/e* 326 (M^+, base peak, 100), 297 (28), 269 (13), 239 (12). Anal. Calcd for $C_{22}H_{14}O_3$: C, 80.97; H, 4.32. Found: C, 80.73; H, 4.42.

7a,14c-Dihydronaphtho[2,1-*b*]naphtho[1′,2′:4,5]furo-[3,2-*d*]furan-3-ol (2c) (exp no. 4). The compound was prepared from 2,6-DHN: mp 206 °C (from benzene); IR (KBr, cm^{-1}) 3440 (broad, a shoulder at 3324, ν_{OH}) 1627, 1602, 1525, 1386, 1214, 1056, 811, 746; UV (acetonitrile) 244 (4.13), 269 (3.85), 277 (3.90), 279 (3.89), 345 (3.79); ^1H NMR (250 MHz) δ 5.8 (d, 1H, ArC*H*Ar), 7.1–7.3 (m, 6H), 7.5–7.6 (m, 2H), 7.9 (t, 2H), 8.2 (d, 1H), 8.3 (d, 1H), 9.6 (s, 1H, O*H*). A signal at 9.6 ppm disappeard upon addition of D_2O; ^{13}C NMR (62.9 MHz, Only signals separated clearly are shown.) δ 48.8 (d, Ar*C*HAr), 110.3, 111.8, 112.0, 114.5, 118.9, 119.3, 123.2, 123.6, 124.4, 125.0, 126.7, 128.3, 128.9, 129.6, 129.9, 130.3, 131.3, 153.2, 153.6, 155.8 (The last three were assigned to the aromatic *C*'s adjacent to O atom. The signal for ArO*C*HOAr is in the aromatic region.); MS *m/e* 326 (M^+, base peak, 100), 297 (40), 239 (25). Anal. Calcd for $C_{22}H_{14}O_3$: C, 80.97; H, 4.32. Found: C, 80.79; H, 4.39.

7a,14c-Dihydronaphtho[2,1-*b*]naphtho[1′,2′:4,5]furo-[3,2-*d*]furan-2-ol (2d) (exp. no. 9). The compound was prepared from 2,7-DHN. The reaction conditions were shown in Table 1 (no. 9): mp 283 °C (from benzene); IR (KBr, cm^{-1}) 3250 (broad, ν_{OH}) 1625, 1590, 1580, 1515, 1255, 1050, 810, 740; UV (acetonitrile) 241 (4.17), 285 (3.86), 293 (3.90), 322 (3.79), 330 (3.81); ^1H NMR (400 MHz) δ 5.74 (d, 1H, J = 5.86, ArC*H*Ar), 6.96 (d, 1H, J = 8.78, H_3), 7.00 (d, 1H, J = 8.79, H_6), 7.24 (d, 1H, J = 5.86, ArOC*H*OAr), 7.31 (d, 1H, J = 8.79, H_9), 7.36 (t, 1H, H_{12}), 7.54 (t, 1H, H_{13}), 7.59 (s, 1H, H_1), 7.69 (d, 2H, J = 8.80, H_5); 7.73 (d, 1H, J = 8.79, H_4), 7.87 (d, 1H, J = 8.79, H_{10}), 7.90 (d, 1H, J = 8.42, H_{11}), 8.38 (d, 1H, J = 8.43, H_{14}), 9.84 (s, 1H, O*H*). The signal at 9.84 ppm disappeared upon addition of D_2O; ^{13}C NMR (100 MHz) δ 48.7 (d, Ar*C*HAr), 105.7, 108.4, 112.1, 114.7, 116.0, 117.2, 119.2, 123.5, 124.0, 124.5, 127.0, 129.1, 129.8, 130.1, 130.4, 130.5, 130.7 (d, *C*-H in naphthalene ring + ArO*C*HOAr), 131.9, 155.9, 156.3, 156.4 (s, naphthalene ring *C*); MS *m/e* 326 (M^+, base peak, 100), 297 (30), 239 (8); Anal. Calcd for $C_{22}H_{14}O_3$: C, 80.97; H, 4.32. Found: C, 80.88; H, 4.34.

7a,9a,16c,20c-Tetrahydronaphtho[2,1-*b*:3,4-*b*′]bisnaphtho[1′,2′:4,5]furo[3,2-*d*]furan (3). Method a: The compound was prepared from **1** with 2,3-DHN by a similar procedure as for the typical one (no. 2 in Table 1). **Method b:** The compound was prepared from **7** and 2-naphthol. The reaction conditions are shown in Table 1 (no. 3): 349 °C dec; IR (KBr, cm^{-1}) 1620, 1590, 1575, 1525 (naphthalene ring), 1260, 1240, 1065, 1050, 805, 740 (characteristic of 1,2-disubstituted naphthalene); UV (acetonitrile) 225 (5.00), 283 (4.07), 293 (4.10), 305 (4.06), 334 (4.06); ^1H NMR (400 MHz, pyridine-d_5) δ 5.90 (d, 2H, J = 5.49, H_{16c} + H_{20c}), 7.32–7.40 (m, 8H, H_3 + H_{14} + H_6 + H_{11} + H_{18} + H_{19} + H_{7a} + H_{9a}), 7.53 (t, 2H, H_2 + H_{15}), 7.89–7.94 (m, 4H, H_4 + H_{13} + H_5 + H_{12}), 8.31–8.35 (m, 4H, H_1 + H_{16} + H_{17} + H_{20}); ^{13}C NMR (100 MHz, pyridine-d_5) [Because of low solubility of **3** in pyridine (and other solvents), a clear spectrum could not be obtained.] δ 50.3 (Ar*C*HAr) 112.6, 116.7, 123.0, 124.0, 124.4, 124.6, 125.6, 127.5, 129.8, 131.4, 135.0, 136.0, 149.3, 150.4; MS *m/e* 492 (M^+, base peak, 100), 179 (26); Anal. Calcd for $C_{34}H_{20}O_4$: C, 82.91; H, 4.09. Found: C, 82.69; H, 4.19.

7a,10c,17a,20c-Tetrahydronaphtho[2,1-*b*:6,5-*b*′]bisnaphtho[1′,2′:4,5]furo[3,2-*d*]furan (4). Method a: The compound was prepared from **1** and 2,6-DHN by a similar procedure as for the typical one (no. 5 in Table 1). **Method b:** The compound was prepared from **8** and 2-naphthol. The reaction conditions are shown in Table 1 (no. 7): 357 °C dec; IR (KBr, cm^{-1}) 1620, 1595, 1530, 1250, 1050, 800, and 740 (characteristic of 1,2-disubstituted naphthalene); UV (acetonitrile) 223 (5.02), 281 (4.22), 292 (4.20), 335 (4.04), 353 (4.04); ^1H NMR (400 MHz) δ 5.94 (d, 2H, J = 5.86, H_{10c} + H_{20c}), 7.23–7.31 (m, 6H, H_3 + H_{13} + H_6 + H_{16} + H_{7a} + H_{17a}), 7.40–7.43 (m, 4H, H_2 + H_{12} + H_9 + H_{19}), 7.82–7.84 (m, 4H, H_4 + H_{14} + H_5 + H_{15}), 8.20 (d, 2H, J = 8.42, H_1 + H_{11}), 8.41 (d, 2H, J = 8.80, H_{10} + H_{20}); ^{13}C NMR (100 MHz) δ 49.0 (d, Ar*C*HAr), 112.0, 112.8, 114.6, 118.7, 120.5, 123.35, 123.44, 126.1, 126.7, 127.0, 129.1, 129.8, 130.7, 154.0, 155.8 (The last two were assigned to the aromatic *C*'s adjacent to the O atom. The signal for ArO-*C*HOAr is in the aromatic region.); MS *m/e* 492 (M^+, base peak, 100), 463 (12), 246 (8). Anal. Calcd for $C_{34}H_{20}O_4$: C, 82.91; H, 4.09. Found: C, 82.58; H, 4.20.

Mixture of 7a,13a,20c,20g-Tetrahydronaphtho[2,1-*b*:7,8-*b*′]bisnaphtho[1′,2′:4,5]furo[3,2-*d*]furan (5) and 7a,-11b,18a,20c-Tetrahydronaphtho[2,1-*b*:7,6-*b*′]bisnaphtho-[1′,2′:4,5]furo[3,2-*d*]furan (6). A mixture of **5** and **6** was obtained from **1** and 2,7-DHN at 60 °C (exp. no 9). An attempted separation of **5** from **6** was failed due to low solubility in common organic solvents: 349 °C dec; IR (KBr, cm^{-1}) 1620, 1590, 1575, 1515, 1250, 1055, 800, 740; ^1H NMR (400 MHz) δ 5.79 (d, 0.75H, J = 6.60, H_{11b} for **6**), 5.82 (d, 0.75H, J = 5.87 H_{20c} for **6**), 6.26 (d, 0.50H, J = 5.50, H_{20c} + H_{20g} for **5**), 7.12 (d, 0.50H, J = 8.42 for **5**), 7.14 (d, 0.75H, J = 8.43, H_9 for **6**), 7.21 (d, 1.50H, J = 8.80, H_6 + H_{17} for **6**), 7.26 (d, 0.75H, J = 5.87, H_{7a} for **6**), 7.27 (d, 0.75H, J = 6.60, H_{18a} for **6**), 7.29–7.39 (m, 2H), 7.45 (d, 0.50H, J = 8.80 for **5**), 7.50 (t, 0.50H for **5**), 7.55–7.59 (m, 1.50H), 7.66 (t, 0.75H, H_{13} for **6**), 7.70 (s, 0.75H, H_{20} for **6**), 7.77–7.84 (m, 4.00H), 7.88 (d, 1.50H, J = 8.06, H_4 + H_{15} for **6**), 7.92 (d, 0.50H, J = 8.42 for **5**), 8.23 (s, 0.75H, H_{11} for **6**), 8.33 (d, 0.75H, J = 8.42, H_{12} for **6**), 8.36 (d, 0.75H, J = 8.42, H_1 for **6**). Proton ratio Ar*H*/ArC*H*Ar = 16:2; ^{13}C NMR (100 MHz) δ 48.4, 48.5 (d, Ar*C*HAr for **6**), 51.2 (d, Ar*C*HAr for **5**), 109.0, 109.7, 111.6, 113.4, 114.6, 115.0, 118.0, 118.6, 118.7, 119.6, 123.0, 123.1, 123.2, 123.5, 123.6, 125.7, 125.8, 126.0, 126.1, 126.7, 128.3, 128.9, 129.3, 129.4, 129.5, 129.8, 130.1, 130.5, 130.8, 154.8, 155.7, 156.3, 157.0 (The last four signals were assigned to the aromatic *C*'s of **6** adjacent to the O atom), 155.4, 157.9 (these two signals were assigned to the aromatic *C*'s of **5** adjacent to the O atom); MS *m/e* 492 (M^+, base peak, 100), 463 (10), 321 (9). Anal. Calcd for $C_{34}H_{20}O_4$: C, 82.91; H, 4.09. Found: C, 82.92; H, 4.24.

6. Pure **6** was prepared from **1** and 2,7-DHN at room temperature (exp. no. 8). Separation of $\mathbf{6}_{syn}$ from $\mathbf{6}_{anti}$ was

(23) For MOPAC ver. 6.0, Stewart, J. J. P., *OCPE Bull.* **1989**, *9*, 10; Revised as ver 6.01 by Hirano, T. for VAX machines *JCPE Newsletter* **1989**, *1*, 10.

(24) Version 7 of MOPAC System for PC under OS/2, Stewart, J. J. P. Stewart Computational Chemistry, Colorado Springs, CO 1993.

unsuccessful: 351 °C dec (by DSC); IR (KBr, cm^{-1}) 1640, 1590, 1520, 1460, 1060, 810, 740; UV (acetonitrile) 245 (4.44), 281 (4.24), 292 (4.21), 335 (4.10); ^1H NMR (400 MHz) δ 5.79 (d, 1H, J = 6.60, H_{11b}), 5.82 (d, 1H, J = 5.87, H_{20c}), 7.14 (d, 1H, J = 8.43, H_9), 7.21 (d, 2H, J = 8.80, $H_6 + H_{17}$), 7.26 (d, 1H, J = 5.87, H_{7a}), 7.27 (d, 1H, J = 6.60, H_{18a}) 7.34−7.40 (tt, 2H, $H_3 + H_{14}$), 7.58 (t, 1H, H_2), 7.66 (t, 1H, H_{13}), 7.70 (s, 1H, H_{20}), 7.77−7.83 (m, 3H, $H_5 + H_{16} + H_{10}$), 7.88 (d, 2H, J = 8.06, $H_4 + H_{15}$), 8.23 (s, 1H, H_{11}), 8.33 (d, 1H, J = 8.42, H_{12}), 8.36 (d, 1H, J = 8.42, H_1). NOE spectrum (400 MHz): Irradiating a singlet at 8.23 ppm enhanced signals at 8.33 (5.4), 7.86 (12.7), and 5.79 ppm (3.2%) and irradiating a singlet at 7.70 ppm enhanced signals at 8.37 (21.6) and 5.82 ppm (6.0%); ^{13}C NMR (100 MHz) δ 48.4, 48.5 (Both signals were doublet and assigned to Ar*C*HAr), 100.9, 109.7, 111.7, 111.8, 113.5, 114.7, 118.5, 118.7, 118.8, 123.2, 123.4, 123.59, 123.64, 125.9, 126.75, 126.83, 127.5, 128.9, 129.1, 129.4, 129.5, 129.9, 130.1, 130.4, 130.7, 130.8, 154.8, 155.7, 156.3, 157.0 (The last four signals were assigned to the aromatic *C*'s adjacent to the O atom. The signal for ArO*C*HOAr was in the aromatic region.); MS *m/e* 492 (M^+, base peak, 100), 463 (10), 246(8). Anal. Calcd for $C_{34}H_{20}O_4$: C, 82.91; H, 4.09. Found: C, 82.83; H, 4.18.

1,2,5,6-Tetrahydronaphtho[2,1-*b*:3,4-*b*']difuran-1,2,5,6-tetraol (7). To a stirred mixture of water (50 mL), 2,3-DHN (5.00 g, 0.0313 mol), and glyoxal (40%, 50 g, 0.345 mol) was added to 1 N KOH (5 mL) at 20 °C. After 3 h, the mixture was extracted with ether (150 mL × 3). Evaporation of the ether gave **7** (4.8 g, 56%): 140 °C dec; IR (KBr, cm^{-1}) 3300 (broad and strong, ν_{OH}), 1630, 1600, 1530; UV (water) 231 (4.20), 297 (3.67), 332 (3.56); ^1H NMR (250 MHz) δ 5.21 (d, 2H, J = 6.78, ArC*H*), 5.75 (d, 2H, J = 6.36, ArOC*H*), 5.80 (s, 1H, ArCO*H*), 5.92 (s, 1H, ArCO*H*), 7.25−7.41 (q, 2H, Ar*H*), 7.47 (s, 1H, ArOC(O*H*)), 7.57 (s, H, ArOCO*H*), 7.77−7.93 (q, 2H, Ar*H*). Four signals at 5.80, 5.92, 7.47, and 7.57 ppm disappeared upon addition of D_2O; ^{13}C NMR (62.9 MHz) δ 109.8 (ArO*C*(OH)), 123.6, 123.9, 124.9, 127.1, 144.3; MS *m/e* 276 (M^+, base peak, 100), 258 (45), 218 (29); Weight loss by TG analysis below 230 °C: 3.20% at 80−140 °C; 12.50% at 140−230 °C. Anal. Calcd for $C_{14}H_{12}O_6 \cdot {}^1/_2H_2O$: C, 58.94; H, 4.59. Found: C, 58.78; H, 4.72.

1,2,6,7-Tetrahydronaphtho[2,1-*b*:6,5-*b*']difuran-1,2,6,7-tetraol (8). To a stirred mixture of 2,6-DHN (1.00 g, 0.00625 mol) and glyoxal (40%, 10.9 g, 0.0752 mol) was added to 1 N KOH (2 mL) at 18−20 °C. After stirring for 5 h, precipitates formed were collected by filtration and washed with water and hexane and dried to give **8** (1.93 g, 99%): mp 90.3 °C (from hexane), 180 °C dec; IR (KBr, cm^{-1}) 3300 (broad and strong, with a shoulder at 3500, ν_{OH}), 1600, 1535, 800; UV (water) 228 (4.23), 266 (3.61), 276 (3.65), 287 (3.51), 360 (3.54); ^1H NMR (250 MHz) δ 5.19 (d, 2H, J = 5.7, ArC*H*Ar), 5.65 (d, 2H, J = 5.7, ArOC*H*), 5.77 (s, 1H, ArCO*H*), 5.89 (s, 1H, ArCO*H*), 7.15 (d, 2H, J = 8.8, Ar*H*), 7.30 (s, 1H, ArOC(O*H*)), 7.40 (s, 1H, ArOC(O*H*)), 7.82 (d, 2H, J = 8.8, Ar*H*); four signals at 5.77, 5.89, 7.30, and 7.40 ppm disappeared upon addition of D_2O; ^{13}C NMR (62.9 MHz) δ 77.2 (ArCH), 108.3 (ArO*C*(OH)), 113.3, 120.7, 125.5, 126.4, 154.7; MS *m/e* 276 (M^+, 45), 258 (base peak, 100), 240 (77), 200 (20); weight loss by TG analysis below 220 °C: 11.63% at 80−140 °C; 11.50% at 160−220 °C. Anal. Calcd for $C_{14}H_{12}O_6 \cdot 2H_2O$: C, 53.84; H, 5.16. Found: C, 53.87; H, 5.18.

Heat Treatment of 8. Compound **8** was heated up to 220 °C in N_2 at a rate of 25 °C/min: IR (KBr, cm^{-1}) 1800 (broad and strong, $\nu_{C=O}$ of lactone), 1600, 1530. The absorption observed at 3300 cm^{-1} in **8** disappeared.

1,2,9,10-Tetrahydronaphtho[2,1-*b*:7,8-*b*']difuran-1,2,9,-10-tetraol (9). Compound **9** was prepared in a yield of 60% by a similar method described in the preparation of **7**; the reaction conditions were shown in Table 1 (no. 12): 135 °C dec; IR (KBr, cm^{-1}) 3300 (broad and strong, ν_{OH}), 1620, 1580, 1510; UV (water) 229 (4.21), 298 (2.57), 331 (3.42); ^1H NMR (250 MHz) δ 5.22−5.73 (m, 5H, 2H for ArC*H* + 2H for ArOC*H* + 1H for ArCO*H*), 6.79−7.04 (m, 3H, 2H for Ar*H* + 1H for ArCO*H*), 7.30−7.89 (m, 3H, 2H for Ar*H* + 1H for ArOCO*H*), 9.57−9.93 (m, 1H, ArOCO*H*). The proton ratio changed from 5:3:3:1 to 4:2:2:0 upon addition of D_2O; ^{13}C NMR (62.9 MHz) δ 65.7, 77.6 (Ar*C*H), 108.6, 110.2 (ArO*C*(OH)), 116.6, 117.4, 118.3, 122.3, 124.0, 126.2, 130.1, 133.0, 153.1, 159.3; MS *m/e* 276 (M^+, 100), 258 (82); weight loss by TG analysis below 230 °C: 3.50% at 80−140 °C; 12.45% at 140−230 °C. Weight loss by calculation: 3.16% for elimination of $^1/_2H_2O$, 12.63% for elimination of $2H_2O$. Anal. Calcd for $C_{14}H_{12}O_6 \cdot {}^1/_2H_2O$: C, 58.94; H, 4.59. Found: C, 58.47; H, 4.97. There was a little difference between calculated and observed values for **9**, due to instability of the hydrate.

1,2,8a,15c-Tetrahydro-2-oxofuro[2',3':7,8]naphtho[2,1-*b*]naphtho[1',2':4,5]furo[3,2-*d*]furan (10). Methanesulfonic acid (4 mL) was added dropwise to **9** (0.5 g, 0.00325 mol) and 2-naphthol (1.2 g, 0.00833 mol) in DME (20 mL). After stirring at room temperature for 24 h, precipitates formed were collected by filtration and washed successively with acetone, water, and hexane, and then dried to give **10** (0.2 g, 21%): mp 273 °C; IR (KBr, cm^{-1}) 1790 (strong, lactone) 1625, 1579, 1537, 1224, 1068, 844, 806; UV (acetonitrile) 244 (4.24), 280 (3.82), 292 (3.85), 321 (3.76), 335 (3.76); ^1H NMR (400 MHz) (Each signal was assigned by $^1H-^1H$ 2D-COSY NMR and $^1H-^1H$ NOESY NMR) δ 4.48−4.67 (q, 2H, CH_2), 5.72 (d, 1H, J = 5.50, H_{15c}), 7.11 (d, 1H, J = 8.8, H_4), 7.25 (d, 1H, J = 5.12, H_{8a}), 7.26−7.35 (m, 2H, $H_{13} + H_{14}$), 7.44 (d, 1H, J = 8.79, H_7), 7.45 (d, 1H, J = 8.79, H_{10}), 7.49 (d, 1H, J = 8.80, H_{15}), 7.89 (d, 1H, J = 8.79, H_5), 7.92 (d, 1H, J = 8.79, H_{12}), 7.94 (d, 1H, J = 8.80, H_{11}), 8.02 (d, 1H, J = 9.16, H_6); NOE (400 MHz) irradiation of a singlet at 5.72 ppm enhanced signals at 4.48−4.67 (5.9), 7.25 (20.5), and 7.49 ppm (1.5%); ^{13}C NMR (100 MHz) δ 34.9 (CH_2), 49.0 (d, Ar*C*HAr), 109.3, 110.3, 112.4, 113.9, 115.4, 116.8, 118.5, 122.0, 123.6, 126.8, 127.5, 127.6, 129.3, 129.9, 130.3, 130.9, 131.3, 131.8 (aromatic *C*'s + ArO*C*HOAr), 153.7, 155.4, 157.3 (the last three; 3 aromatic *C*'s adjacent to the O atom), 174.3 (*C*OO); MS *m/e* 366 (M^+, base peak, 100), 237 (53), 321 (34). Anal. Calcd for $C_{24}H_{14}O_4$: C, 78.68; H, 3.85. Found: C, 78.50; H, 4.02.

1,2,6,7-Tetrahydro-2,7-dioxonaphtho[2,1-*b*][6,5-*b*']difuran (11). Methanesulfonic acid (4 mL) was added to **8** (0.57 g, 0.00180 mol) in DME (15 mL). After stirring at 40 °C for 24 h, precipitates were treated similarly as in the procedure for **10** to give **11** (0.14 g, 33%): 366 °C dec; IR (KBr, cm^{-1}) 1800−1780 (strong, $\nu_{C=O}$), 1595, 1535, 1240, 1110, 845, 755; UV (acetonitrile) 237 (4.00), 271 (3.60), 282 (3.67), 293 (3.50), 338 (3.44), 353 (3.49); ^1H NMR (400 MHz) δ 4.27 (s, 4H, CH_2), 7.57 (d, 2H, J = 9.1, Ar*H*), 7.79 (d, 2H, J = 8.8, Ar*H*); ^{13}C NMR (100 MHz) δ 32.2 (CH_2), 112.7, 124.7 (aromatic *C*H), 119.3, 126.0, 150.6 (aromatic *C*), 174.5(*C*OO); MS *m/e* 240 (M^+, base peak, 100), 212 (78), 184 (89). Anal. Calcd for $C_{14}H_8O_4$: C, 70.00; H, 3.33. Found: C, 69.72; H, 3.41.

1,2,9,10-Tetrahydro-2,9-dioxonaphtho[2,1-*b*][7,8-*b*']difuran (12). Compound **12**, dehydrated form of **9**, was prepared in a yield of 75% by a similar method described in the preparation of **11**; the reaction conditions are shown in Table 1 (no. 15): 403 °C dec; IR (KBr, cm^{-1}) 1800−1780 (strong, $\nu_{C=O}$ of lactone), 1620, 1575, 1545, 1240, 1035, 840, 760; UV 241 (4.13), 291 (3.65), 302 (3.66); ^1H NMR (400 MHz) δ 4.44 (s, 4H, CH_2), 7.45 (d, 2H, J = 8.6, Ar*H*), 8.05 (d, 2H, J = 8.6, Ar*H*); MS *m/e* 240 (M^+, base peak, 100), 184 (65). Anal. Calcd for $C_{14}H_8O_4$: C, 70.00; H, 3.33. Found: C, 69.82; H, 3.47.

JO941994C