J. Org. Chem. 1987, *52*, 2653–2656

(2 × 10 mL). The combined ether extracts were washed with water and dried over $MgSO_4$. The solvent was removed by careful distillation. The resulting products showed the same properties as those obtained by thermolysis.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF Aktiengesellschaft in Ludwigshafen for financial support. We are grateful to Dr. P. Kunzelmann for his help with the NMR spectra. W.S. thanks the Studienstiftung des Deutschen Volkes for a stipend.

Note added in proof: After completion of this paper, J. Dressel and L. A. Paquette informed us about their successful synthesis of **2**.[5b] According to their findings the thermal behavior of **2** is in line with the predictions of our calculations.

Supplementary Material Available: ^{1}H NMR spectrum and ^{1}H shift-correlated NMR spectrum (COSY) of **33** as well as the IR spectrum of the pyrolysis products of the sodium salt of **19** (4 pages). Ordering information is given on any current masthead page.

[3.3]Orthocyclophanes with Facing Benzene and Naphthalene Rings[1]

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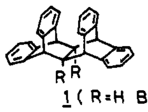
Dibenzo-, dinaphtho-, and benzonaphthobicyclo[4.4.1]undecan-11-ones **3**, **4**, and **6a** were converted into [3.3]orthocyclophanes **8–10** and **12** by the reaction of the carbonyl group at the bridge with ethylene and propylene glycol, ethane-1,2-dithiol, and Grignard reagents. Compared with those of the corresponding ketones, upfield shifts of aromatic protons of **8–10** and **12** were observed in ^{1}H NMR spectra. Their electronic spectra have an absorption tail that extends to about a 10 nm higher wavelength. X-ray crystallography of dibenzo derivatives **8a** and **9a** disclosed that the closest intramolecular distances of two benzene rings is 3.03–3.07 Å and the dihedral angle between two benzenes is 25°.

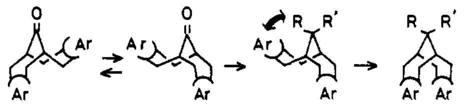
Meta- and paracyclophanes have attracted much attention in the last two decades because of their layered structures with facing aromatic rings.[2] On the other hand, orthocyclophanes generally possess a rather flattened structure and have been less studied. Several compounds that contain [2.2]- and [3.3]orthocyclophane moieties are known;[3] however, there are only a few examples of orthocyclophanes that exhibit a "π–π" interaction of the two facing aromatic rings. Janusene (1)[4] and the related compound 2[5] are [3.3]orthocyclophanes whose electronic spectra show a characteristic band that reflects a throughspace interaction of the two facing benzene rings.



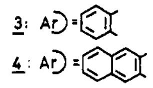
1 (R=H Br)

2

We reported the preparation of dibenzo- (3) and dinaphtho[4.4.1]undecan-11-one (4), which are flexible and exist as two equivalent conformers with $\Delta G^{\ddagger} = 10–15$ kcal mol^{-1}.[7] The introduction of bulky substituents onto the C1 bridge of **3** resulted in increased repulsion between the substituents and the two benzene rings, forcing the rings to take a facing conformation (eq 1). We describe the preparation and characterization of [3.3]orthocyclophanes that have facing benzene and naphthalene rings.



(1)



Results and Discussion

Preparation of [3.3]Orthocyclophanes. Dibenzo- and dinaphthobicyclo[4.4.1]undecan-11-one (**3** and **4**) were prepared as reported.[6] Benzocycloheptenonedicarboxylate **5a** and its naphtho analogue **5b** were needed to prepare benzo–naphtho derivative **6a**. Although some preparative methods have been reported,[7] we synthesized **5a** and **5b** by the reaction of the bis(bromomethyl)arenes **7a** and **7b**

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(1) A part of this paper was published in a preliminary communication: Mataka, S.; Takahashi, K.; Hirota, T.; Takuma, K.; Kobayashi, H.; Tashiro, M. *J. Chem. Soc., Chem. Commun.* **1985**, 973.

(2) Keehn, P. M.; Rosenfeld, S. M. *Cyclophanes*; Organic Chemistry (N.Y.) Monograph 45; Academic: New York, 1983; Vol. I and II.

(3) For example: (a) Gleiter, J. H. *J. Chem. Soc.* **1961**, 3741. (b) Toyoda, T.; Otsubo, T.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1972**, 321. (c) Collins, D. J.; Roberts, D. B.; Sugowalz, G.; Wells, D.; Sasse, W. H. F. *Tetrahedron Lett.* **1972**, 321.

(4) (a) Cristol, S. J.; Lewis, D. S. *J. Am. Chem. Soc.* **1967**, *89*, 1476. (b) Macintyre, W. M.; Tench, A. H. *J. Org. Chem.* **1973**, *38*, 130.

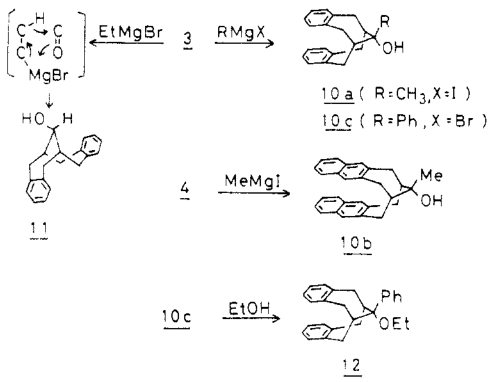
(5) Prinzbach, H.; Sedelmeier, G.; Kruger, C.; Goddard, R.; Martin, H.-D.; Gleiter, R. *Angew. Chem.* **1978**, *90*, 297.

(6) Mataka, S.; Takahashi, K.; Hirota, T.; Takuma, K.; Kobayashi, H.; Tashiro, M.; Imada, K.; Kuniyoshi, M. *J. Org. Chem.* **1986**, *51*, 4618.

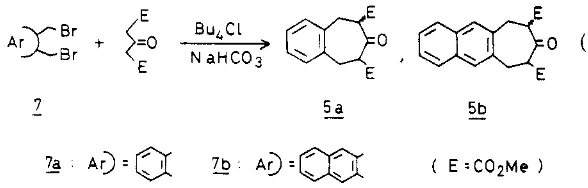
(7) For example: (a) Jones, W. M.; LaBar, B. A.; Brinker, V. H.; Gebert, P. H. *J. Am. Chem. Soc.* **1977**, *99*, 6379. (b) Allinger, N. L.; Skybalo, W. *J. Org. Chem.* **1962**, *27*, 1962.

0022-3263/87/1952-2653$01.50/0

Scheme I

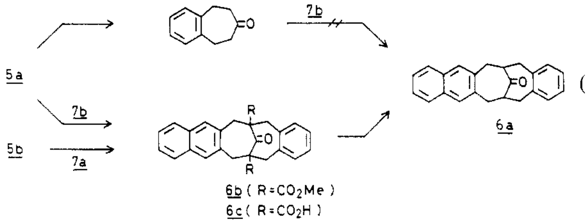


with dimethyl 3-oxoglutarate under phase-transfer-catalyzed conditions with sodium hydrogen carbonate as a base (eq 2). Compounds **5a** and **5b** were obtained as a mixture of stereoisomers in 43 and 49% yields, respectively. The ratios of isomers were determined by ^{1}H NMR as 3:1 in **5a** and 2:1 in **5b**. Both diastereomers of **5a** and one of **5b** could be isolated by fractional recrystallization from hexane. These diastereomers were readily interconvertible, and on melting, each one gave a mixture of the two diastereomers. Identification of these isomers was not made.



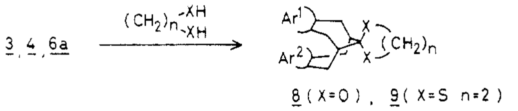
(2)

Bicyclo ketone **6a** was prepared by both routes shown in eq 3. Diester **6b** was obtained in the same yields (60 and 61%) by reaction of **5a** with **7b** and by that of **5b** with **7a**. Hydrolysis of **6b** and pyrolysis of the dicarboxylic acid **6c** gave **6a** in 40% yield from **6b**.



(3)

In order to transform the bridge carbonyl group into a bulkier one, the ketones were converted to acetals and dithioacetals (eq 4). Although **6b** did not form acetals, ketones **3**, **4**, and **6a** gave the corresponding acetals **8a–d** and dithioacetals **9a–c** in the reaction with ethylene glycol, propylene glycol, and ethane-1,2-dithiol. The low yield of **8d** resulted from hydrolysis on workup.



(4)

8a: Ar^1 = B, Ar^2 = B, n = 2, Y = 79%
b Ar^1 = B, Ar^2 = B, n = 3, Y = 89%
c: Ar^1 = N, Ar^2 = N, n = 2, Y = 70%
d: Ar^1 = B, Ar^2 = N, n = 2, Y = 24%
9a: Ar^1 = B, Ar^2 = B, Y = 96%
b: Ar^1 = N, Ar^2 = N, Y = 96%
c: Ar^1 = B, Ar^2 = N, Y = 62%

B and N indicate benzo and 2,3-naphtho annelation

The alkylation and arylation of **3** and **4** with Grignard reagents proceeded as shown in Scheme I.

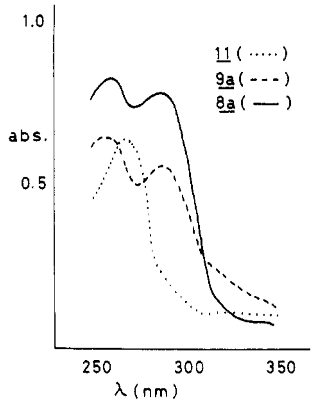
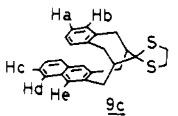


Figure 1. Diffuse reflectance spectra of **8a**, **9a**, and **11**.

Reaction of **3** or **4** with CH_3MgI gave alcohols **10a** and **10b** in 79 and 65% yields, respectively. On the other hand, reaction of **3** with C_2H_5MgBr afforded **11**[6] in 79% yield. Reaction of **3** with PhMgBr gave **10c** in 65% yield. Compound **10c** afforded a 3.3:1 mixture of **10c** and **12** when refluxed in ethanol for 25 h.

^{1}H NMR Spectra. The signals of aromatic protons of **8a–c**, **9a,b**, **10a,b**, and **12** appeared about δ 0.3–0.5 upfield from those of the parent ketones **3** and **4**. In the spectrum of the mixed type **9c**, H_a of the benzene ring was shifted farther and was observed as a multiplet centered at δ 6.36, because it is positioned just above the facing naphthalene ring. On the other hand, H_c and H_d of the naphthalene ring, which are situated out of the effective region of the ring current of the facing benzene ring, appeared at about δ 0.2 lower field than those of **9b**, but still δ 0.2 higher than those of ketone **4**. Signals of H_b and H_e were observed at the position similar to those of the corresponding protons in **9a** and **9b**, respectively. Benzyl signals were observed as an ABX pattern with J_{gem} = 15–16 and J_{vic} = 0–3 and 5–6 Hz, respectively. The observed J_{vic} values are in accord with J_{ae} (<2 Hz) and J_{ee} (6.0–6.7 Hz) of 1,1-disubstituted 4,5-benzocycloheptenes[8] but differ from J_{aa} (11.6–13.0 Hz).



9c

Electronic Spectra. Absorption spectra were measured in $CHCl_3$. Compared with the spectra of the ketones **3**, **4**, and **6a**, enhanced absorption was observed at about a 10 nm higher wavelength in the spectra of **8a–c**, **9a–c**, **10a–c**, and **12**. This absorption is ascribed to a π–π through-space interaction between two facing aromatic rings as is characterized in **1** and **2**. Diffuse reflectance spectra of solid **8a** and **9a** showed two absorption maxima around 260 and 290 nm, while that of **11**, which exists in a chair-boat conformation,[6] showed only one peak around 270 nm as shown in Figure 1. The band at longer wavelength indicates the presence of a through-space interaction in solid phase. Therefore, [3.3]orthocyclophanes **8–10** and **12** have the same twin-chair conformation in both solid and solution phases.

Crystal and Molecular Structure of 8a and 9a. X-ray crystallography showed the nearest approach of the two benzene rings in **8a** and **9a** are 3.03–3.07 Å, while the largest separation of the rings is 4.1 Å. The dihedral angle between the planes of two benzene rings is ca. 25°. These

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[8] Kabuss, H.; Schmid, H. G.; Freibolin, H.; Faisst, W. *Org. Magn. Reson.* **1969**, *1*, 451.

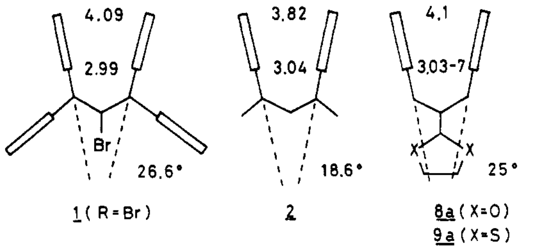

Figure 2. Structural data of 1 (R = Br), 2, 8a, and 9a.

data are depicted in Figure 2 together with those of 1 (R = Br)[4] and 2.[5] The crystal structures of 8a and 9a resemble that of janusene (1) rather than 2.

Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded on a Nippon Bunko A-102 spectrophotometer as KBr pellets. ^1H and ^{13}C NMR (internal Me_4Si) spectra were taken on a Nippon Denshi JEOL FT-100 NMR spectrometer in deuteriochloroform unless otherwise stated. Mass spectra were recorded on a Nippon Denshi JMS-O1SG-2 mass spectrometer at 75 eV using a direct-inlet system. Electronic spectra were taken on a Hitachi 220 spectrophotometer in chloroform and diffuse reflectance spectra on a Hitachi 330 spectrophotometer. Column chromatography was carried out on silica gel (Wako gel, C-300).

Dimethyl 1,2,4,5-Tetrahydro-3-oxobenzo[*d*]cycloheptene-2,4-dicarboxylate (5a). To a vigorously stirred mixture of 7a (10.1 g, 38 mmol), Bu_4NBr (7.3 g, 22 mmol), a 5% aqueous $NaHCO_3$ solution (500 mL), and CH_2Cl_2 (50 mL) was added dropwise at room temperature a solution of dimethyl 3-oxoglutarate (12.8 g, 73 mmol) in CH_2Cl_2 (50 mL). After 9 h, the organic layer was separated, dried, and evaporated in vacuo, yielding a residue that was recrystallized from hexane to give 5a [4.56 g, 43%; mp 80–104 °C] as a mixture of colorless needles (5a-1) and prisms (5a-2). Small amounts of 5a-1 and 5a-2 were isolated by fractional recrystallization from hexane. 5a-1: mp 103–110 °C; IR 1740, 1690 cm^{-1}; ^1H NMR δ 2.9–3.4 (m, 4 H), 3.64 (s, 6 H), 3.7–4.0 (m, 2 H), 7.16 (s, 4 H); MS, *m/e* 276 (M^+). Anal. Calcd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84. Found: C, 65.14; H, 5.83. 5a-2: mp 93–100 °C; IR 1740, 1690 cm^{-1}; ^1H NMR δ 3.0–3.7 (m, 6 H), 3.74 (s, 6 H), 7.20 (s, 4 H); MS, *m/e* 276 (M^+). Anal. Calcd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84. Found: C, 65.22; H, 5.79.

Dimethyl 1,2,4,5-Tetrahydro-3-oxonaphtho[2,3-*d*]cycloheptene-2,4-dicarboxylate (5b). Compound 5b was prepared by dropwise addition of a solution of dimethyl 3-oxoglutarate (6.13 g, 35 mmol) in CH_2Cl_2 (40 mL) to a mixture of 7b (6.22 g, 20 mmol), Bu_4NBr (3.72 g, 12 mmol), 8% aqueous $NaHCO_3$ (100 mL), and CH_2Cl_2 (60 mL) and stirring the mixture for 40 h. The reaction mixture was worked up by using the same method as for 5a, and recrystallization from ethanol gave 5b as colorless needles: 3.17 g, 49%; mp 142–146 °C; IR 1730, 1710 cm^{-1}; ^1H NMR δ 3.2–4.0 (m, 6 H), 3.64 (s, 4.5 H), 3.76 (s, 1.5 H), 7.36–7.52 (m, 2 H), 7.66 (br s, 2 H), 7.70–7.80 (m, 2 H); MS, *m/e* 326 (M^+). Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.92; H, 5.56. Found: C, 69.81; H, 5.56. One of the two diastereomers of 5b was obtained by fractional recrystallization from hexane: mp 150–153 °C; ^1H NMR δ 3.0–3.6 (m, 4 H), 3.66 (s, 6 H), 3.7–4.1 (m, 2 H), 7.36–7.50 (m, 2 H), 7.66 (br s, 2 H), 7.70–7.80 (m, 2 H); MS, *m/e* 326 (M^+). Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.92; H, 5.56. Found: C, 70.25; H, 5.54.

Dimethyl Benzo[*c*]naphtho[2,3-*h*]-11-oxobicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylate (6b). To a vigorously stirred mixture of Bu_4NCl (2.40 g, 8.6 mmol), 23% aqueous NaOH (45 mL), and CH_2Cl_2 (30 mL) was added dropwise at room temperature a CH_2Cl_2 solution (80 mL) of 5a (4.21 g, 15 mmol) and 7b (4.73 g, 15 mmol). After being stirred at room temperature for 25 h, the organic layer was separated, dried, and evaporated in vacuo, leaving a residue which, after recrystallization from a 5:1 mixture of ethanol and benzene, gave 6b as colorless prisms: 3.87 g, 60%; mp 242–243 °C; IR 1735, 1690 cm^{-1}; ^1H NMR δ 2.4–4.0 (br peak, 8 H), 3.68 (s, 6 H), 6.8–7.9 (br peak, 10 H); MS, *m/e* 428 (M^+). Anal. Calcd for $C_{27}H_{24}O_5$: C, 75.68; H, 5.65. Found: C, 75.63; H, 5.57. Compound 6b (1.00 g, 61%) was also obtained by the reaction of 5b (1.05 g, 4.0 mmol) with 7a (1.28 g, 4.0 mmol) in the presence of Bu_4NCl (0.69 g, 2.5 mmol) and 23% aqueous NaOH (8.6 mL).

Benzo[*c*]naphtho[2,3-*h*]-11-oxobicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylic Acid (6c). After a mixture of 6b (3.00 g, 7.0 mmol), KOH (1.89 g), ethanol (100 mL), and water (100 mL) had been refluxed for 2.5 h, it was poured into water (300 mL), acidified with concentrated HCl to pH 1, and allowed to stand overnight. The precipitate was filtered and dried, giving crude 6c (2.71 g). Recrystallization from a mixture of water and acetic acid gave 6c as colorless prisms: mp 280 °C dec; IR 1700 cm^{-1}. Anal. Calcd for $C_{25}H_{20}O_5$: C, 74.99; H, 5.03. Found: C, 74.87; H, 5.15.

Benzo[*c*]naptho[2,3-*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one (6a). Crude 6c (1.00 g) was heated at 280 °C until gas evolution ceased, and it was triturated with CH_2Cl_2. Insoluble materials were filtered off, and the filtrate was chromatographed with chloroform as an eluent, affording 6a which, on recrystallization from benzene, gave colorless needles: 0.31 g; mp 190–192 °C; IR 1700 cm^{-1}; UV λ_{max} (log ϵ) 263 nm (3.61), 272 (3.67), 281 (3.64), 292 (3.42), 307 (2.56), 320 (2.29); ^1H NMR δ 2.4–3.6 (br peak, 10 H), 7.16 (s, 4 H), 7.34–7.48 (m, 2 H), 7.60 (br s, 2 H), 7.68–7.78 (m, 2 H); MS, *m/e* (M^+). Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found: C, 88.28; H, 6.54.

Dibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one Ethylene Acetal (8a). A mixture of 3 (0.70 g, 2.7 mmol), ethylene glycol (0.20 g, 3.2 mmol), and a catalytic amount of *p*-TsOH in benzene (6 mL) was refluxed with a Dean–Stark water separator for 4 h. After cooling, the precipitate was filtered and recrystallized from benzene to give 8a (0.65 g, 79%) as colorless prisms: mp 221–222 °C; ^1H NMR δ 2.30 (m, 2 H), 2.68 (dd, *J* = 16, 6 Hz, 4 H), 3.40 (dd, *J* = 16, 3 Hz, 4 H), 4.02 (s, 4 H), 6.66 (s, 8 H); ^{13}C NMR δ 36.4, 42.4, 64.5, 113.5, 125.6, 130.2, 139.4; MS, *m/e* 306 (M^+), 201. Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.55; H, 7.28.

Dibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one Trimethylene Acetal (8b). A mixture of 3 (0.50 g, 1.9 mmol) and trimethylene glycol (0.24 g, 3.1 mmol) in toluene (4 mL) in the presence of a catalytic amount of *p*-TsOH was refluxed for 4 h and treated as was 8a, giving 8b (0.54 g, 89%) as colorless prisms (benzene): mp 235–236 °C; ^1H NMR δ 1.82 (q, *J* = 6 Hz, 2H), 2.64 (dd, *J* = 16, 5 Hz, 4 H), 2.80 (m, 2 H), 3.40 (dd, *J* = 16, 2 Hz, 4 H), 3.99 (t, *J* = 6 Hz, 4 H), 6.64 (s, 8 H); MS, *m/e* 320 (M^+), 262, 215. Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.66; H, 7.59.

Dinaphtho[2,3-*c*; 2′,3′-*h*]bicyclo[4.4]undeca-3,8-dien-11-one Ethylene Acetal (8c). A mixture of 4 (1.00 g, 2.7 mmol), ethylene glycol (0.34 g, 5.5 mmol), and a catalytic amount of *p*-TsOH in toluene (25 mL) was heated at reflux for 3 h, and the solvent was evaporated in vacuo to afford a residue, which was recrystallized from benzene to give 8c (0.79 g, 70%) as colorless needles: mp 325 °C dec; UV λ_{max} (log ϵ) 262 nm (4.06), 272 (4.07), 282 (4.02), 307 (3.19), 323 (2.84), 335 (2.43); ^1H NMR δ 2.44 (m, 2 H), 2.92 (dd, *J* = 16, 6 Hz, 4 H), 3.50 (dd, *J* = 16, 3 Hz, 4 H), 4.00 (s, 4 H), 6.9–7.15 (7, 4 H), 7.12 (br s, 4 H), 7.2–7.4 (m, 4 H); MS, *m/e* 406 (M^+), 251. Anal. Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.68; H, 6.48.

Benzo[*c*]naphtho[2,3-*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one Ethylene Acetal (8d). A mixture of 6a (0.32 g, 1.0 mmol), ethylene glycol (0.10 g, 1.3 mmol), and a catalytic amount of *p*-TsOH in benzene (25 mL) was refluxed for 5 h. After it had cooled, the precipitate was removed by filtration, giving 8d as colorless plates: 0.09 g, 24%; mp 240 °C (in sealed tube); MS, *m/e* 356 (M^+). Anal. Calcd for $C_{25}H_{24}O_2$: C, 84.24; H, 6.78. Found: C, 84.08; H, 6.76.

Dibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one Ethylene Dithioacetal (9a). A mixture of 3 (0.50 g, 1.91 mmol), ethane-1,2-dithiol (1 mL), and $BF_3{\cdot}OEt_2$ (1 mL) in acetic acid (15 mL) was heated at reflux for 1.5 h. After it cooled, the precipitated 9a was filtered and recrystallized from benzene to give colorless needles: 0.62 g, 96%; mp 263–267 °C; ^1H NMR δ 2.70 (br s, 2 H), 2.88 (dd, *J* = 16, 6 Hz, 4 H), 3.34 (s, 4 H), 3.68 (dd, *J* = 16, 2 Hz, 4 H), 6.72 (s, 8 H); MS, *m/e* 338 (M^+), 277. Anal. Calcd for $C_{21}H_{22}S_2$: C, 74.51; H, 6.55. Found: C, 74.67; H, 6.47.

Dinaphtho[2,3-*c*; 2′,3′-*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one Ethylene Dithioacetal (9b). A mixture of 4 (0.30 g, 0.83 mmol), ethane-1,2-dithiol (1 mL), and $BF_3{\cdot}OEt_2$ (1 mL) in acetic acid (13 mL) was heated at reflux for 3 h and treated as was **9a**, giving **9b** (0.35 g, 96%) as colorless prisms (benzene): mp >300 °C; UV λ_{max} (log ϵ) 260 nm (4.12), 271 (4.12), 283 (4.07), 310 (3.23), 325 (2.81), 338 (2.49); ^{1}H NMR δ 2.5–2.8 (m, 2 H), 2.92 (dd, J = 15, 6 Hz, 4 H), 3.33 (s, 4 H), 3.79 (dd, J = 15, 2 Hz, 4 H), 6.9–7.1 (m, 4 H), 7.10 (s, 4 H), 7.1–7.4 (m, 4 H); MS, m/e 438 (M$^+$). Anal. Calcd for $C_{29}H_{26}S_2$: C, 79.4; H, 5.97. Found: C, 79.44; H, 6.03.

Benzo[*c*]naphtho[2,3-*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one Ethylene Dithioacetal (9c). A mixture of **6a** (0.30 g, 1.00 mol), ethane-1,2-dithiol (1 mL), and $BF_3{\cdot}OEt_2$ (1 mL) in acetic acid (8 mL) was heated at reflux for 4 h, giving **9c**: 0.23 g, 62%; mp 280–281 °C; UV λ_{max} (log ϵ) 277 nm (3.70), 290 (3.61), 300 (3.39), 315 (2.70), 330 (2.55); ^{1}H NMR δ 2.7–3.1 (m, 4 H), 3.08 (dd, J = 15, 6 Hz, 2 H), 3.33 (s, 4 H), 3.66 (dd, J = 15, 0 Hz, 2 H), 3.80 (dd, J = 15, 0 Hz, 2 H), 6.3–6.5 (m, 2 H), 7.10 (s, 2 H), 7.2–7.4 (m, 2 H), 7.4–7.6 (m, 2 H); MS m/e 388 (M$^+$). Anal. Calcd for $C_{25}H_{24}S_2$: C, 77.27; H, 6.22. Found: C, 77.48; H, 6.12.

11-Hydroxy-11-methyldibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-diene (10a). To a dry ether solution (2 mL) of methylmagnesium iodide (4.11 mmol) was added dropwise at room temperature a benzene solution (6 mL) of **3** (0.50 g, 1.91 mmol), and the mixture was refluxed for 6 h. Aqueous ammonium chloride (17%, 10 mL) was added to the reaction mixture, and the organic layer was separated, dried, and evaporated in vacuo to afford a solid, which was recrystallized from ethanol to give **10a** (0.42 g, 79%) as colorless needles: mp 203–204 °C; ^{1}H NMR δ 1.60 (s, 4 H), 2.24 (m, 2 H), 2.61 (dd, J = 15, 6 Hz, 2 H), 2.80 (dd, J = 16, 5 Hz, 2 H), 3.28 (dd, J = 16, 3 Hz, 2 H), 3.67 (dd, J = 15, 3 Hz, 2 H), 6.70 (s, 8 H); MS, m/e 278 (M$^+$), 260. Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.96. Found: C, 85.99; H, 8.03.

11-Hydroxy-11-methyldinaphtho[2,3-*c*;2′,3′-*h*]bicyclo[4.4.1]deca-3,8-diene (10b). A mixture of **4** (0.30 g, 0.83 mmol) in dry benzene (20 mL) and methylmagnesium iodide (0.83 mmol) in dry ether (4 mL) was refluxed for 5 h and treated as described above, affording **10b** (0.20 g, 65%) as colorless needles (benzene): mp 300 °C dec; ^{1}H NMR δ 1.52 (s, 4 H), 2.2–2.5 (m, 2 H), 2.86 (dd, J = 15, 6 Hz, 2 H), 3.04 (dd, J = 15, 6 Hz, 2 H), 3.40 (dd, J = 15, 3 Hz, 2 H), 3.78 (dd, J = 15, 3 Hz, 2 H), 6.9–7.1 (m, 4 H), 7.13 (s, 4 H), 7.2–7.4 (m, 4 H); MS, m/e 378 (M$^+$), 205. Anal. Calcd for $C_{28}H_{26}O$: C, 88.85; H, 6.92. Found: C, 89.01; H, 7.01.

11-Hydroxy-11-phenyldibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-diene (10c). A mixture of **3** (0.30 g, 1.14 mmol) in dry benzene (10 mL) and phenylmagnesium bromide (2.46 mmol) in dry ether (10 mL) was refluxed for 5.5 h and then treated with 17% aqueous ammonium chloride (30 mL). The organic layer was separated, dried, and evaporated in vacuo to leave a residue, which was chromatographed using benzene as an eluent giving **10c** (0.25 g, 65%) as colorless needles (cyclohexane); mp 203–205 °C; ^{1}H NMR δ 1.53 (br s, 1 H), 2.7–3.3 (m, 8 H), 3.96 (dd, J = 16, 2 Hz, 2 H), 6.60 (s, 4 H), 6.78 (s, 4 H), 7.16–7.40 (m, 3 H), 7.5–7.7 (m, 2 H); MS, m/e 340 (M$^+$), 322, 231, 217. Anal. Calcd for $C_{25}H_{24}O$: C, 88.20; H, 7.10. Found: C, 88.35; H, 7.09.

11-Hydroxydibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-diene (11). A mixture of **3** (1.00 g, 3.82 mmol) in dry benzene (10 mL) and ethylmagnesium bromide (9.17 mmol) in dry ether (10 mL) was heated at reflux for 5 h and treated as was **10c**, giving **11**^{6} (0.79 g, 79%).

11-Ethoxy-11-phenyldibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-diene (12). After **10c** was refluxed in ethanol for 25 h, the solvent was evaporated in vacuo and the resulting solid was analyzed by ^{1}H NMR. Compound **12** was separated from **10c** through column chromatography, using benzene as an eluant. **12**: mp 239–240 °C; colorlesss prisms (ethanol); ^{1}H NMR δ 0.96 (t, J = 7 Hz, 3 H), 2.6–3.4 (m, 10 H), 3.88 (dd, J = 16, 0 Hz, 2 H), 6.56 (s, 4 H), 6.70 (s, 4 H), 7.1–7.4 (m, 3 H), 7.5–7.6 (m, 2 H); MS, m/e 368 (M$^+$), 322, 217. Anal. Calcd for $C_{27}H_{28}O$: C, 88.00; H, 7.66. Found: C, 88.28; H, 7.67.

X-ray Analyses. All data sets were measured by the $\omega-2\theta$ method on a CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ 0.71073 Å). Structures were refined by the SDP program package.[9] **8a**: orthorhombic space group $P2_1/c2_1/m2_1/n$; a = 7.957 (2) Å, b = 12.485 (4) Å, c = 15.81 (1) Å, V = 1570 (2) Å^3; d(calcd) = 1.295 g·cm^{-3}, d(obsd) = 1.279 g·cm^{-3} for Z = 8; an asymmetric unit consisting of a moiety of the molecule, C9, C10, C11, H91, H101, being on a mirror, therefore 4 molecules in a cell; μ(Mo Kα) = 0.846 cm^{-1}; 1893 unique reflections, solution by direct method (MULTAN 82)[11] and refined by least-squares method, R 0.076, R_w 0.078, unit weight for 109 variables and 1318 reflections with $I \geq 3.0\sigma(I)$; all non-hydrogen atoms anisotropic with hydrogen atoms isotropic. **9a**: orthorhombic space group $Pnma$; a = 15.94 (2) Å, b = 12.639 (2) Å, c = 8.202 (2) Å, V = 1652 (3) Å^3, d(calcd) = 1.360 g·cm^{-3}, d(obsd) = 1.324 g·cm^{-3} for Z = 8; an asymmetric unit consisting of a moiety of a molecule, as above, 4 molecules in a unit cell; μ(Mo Kα) = 3.14 cm^{-1}; 2935 unique reflections, solution by direct method (MULTAN 82)[11] and refined by least-squares method, R 0.068, R_w 0.066, unit weight, for 109 variables and 2090 reflections with $I \geq 3.0\sigma(I)$; all non-hydrogen atoms anisotropic with hydrogen atoms isotropic.

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Supplementary Material Available: Tables of positional parameters, anisotropic and isotropic thermal parameters, and rms amplitudes of thermal vibration, ORTEP drawing, and tables of weighted least-squares planes, bond distances, bond angles, and torsional angles for **8a** and **9a** (24 pages); observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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