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On the Conformation of Benzo-Annelated Bicyclo[4.4.1]undecanes, Bicyclo[5.5.1]tridecanes, and a Bicyclo[5.4.1]dodecane

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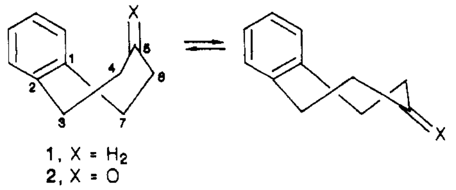
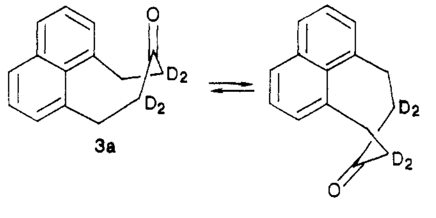
The preparation and conformational analysis of dibenzo[3,4;8,9]bicyclo[4.4.1]undeca-3,8-dienes (**4**), dinaphtho[3,4-*b*;8,9-*b*′]bicyclo[4.4.1]undeca-3,8-dienes (**5**), dinaphtho[3,4,5-*de*;9,10,11-*d′e′*]bicyclo[5.5.1]trideca-3,9-dienes (**6**), and an *unsym*-naphtho[3,4,5-*de*]benzo[9,10]bicyclo[5.4.1]dodeca-3,9-dien-12-one (**7**) are reported. Bicyclo[4.4.1]undecanes **4a**, **4f**, **5a**, and **5c** exist in equilibrium between two chair-boat conformers. Alcohols **4d**, **4e**, and **5e** are in equilibrium between two nonequivalent chair-boat conformers, of which the major, sterically favored conformer has the hydroxy group axial in the boat form. Methyl ether **4g** is fixed in the sterically favored chair-boat form. On the other hand, bicyclo[5.5.1]tridecanes **6a**, **6c**, and **6e** exist in a rigid boat-boat form. The unsymmetrical bicyclo[5.4.1]dodecane **7** is fixed in a chair-boat form in which the seven-membered ring is in the chair form.

Ring inversion is a characteristic behavior of alicyclic compounds, and extensive studies on medium-sized cyclic compounds have been made by dynamic NMR spectroscopy.[1]

Benzocycloheptene (**1**) and 4,5-benzocycloheptenone (**2**) are reported to exist preferentially in the chair conformation and to undergo ring-inversion with $\Delta G^{\ddagger}$ of 10.9 and less than 5 kcal mol^{-1}, respectively.[2] The different inversion $\Delta G^{\ddagger}$ values were attributed to the difference in the ease of wagging motion of the C(5)-methylene and that of the carbonyl group in the chair-to-boat transition step (rotation about the C(4)–C(5) and C(5)–C(6) bonds). On the other hand, 8,9,10,11-tetrahydro-7*H*-cycloocta[*d*,*e*]naphthalen-9-one (**3**)[3,4] interconverts between two boat-form conformers, conceivably via an intermediary twist-boat form afforded by pseudorotation of one end of the peri bridge ($\Delta G^{\ddagger}$ = 12.4 kcal mol^{-1} for **3a**).[3]

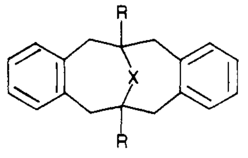


1, X = H_2
2, X = O

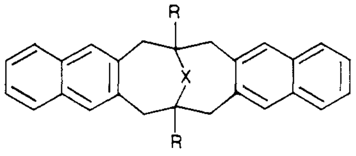


3a

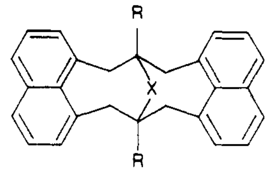
We report here on some conformational studies of related bicyclic compounds, *sym*-dibenzo[3,4;8,9]bicyclo[4.4.1]undeca-3,8-dienes (**4**), dinaphtho[3,4-*b*;8,9-*b*′]bicyclo[4.4.1]undeca-3,8-dienes (**5**), dinaphtho[3,4,5-*de*;9,10,11-*d′e′*]bicyclo[5.5.1]trideca-3,9-dienes (**6**), and *unsym*-naphtho[3,4,5-*de*]benzo[9,10]bicyclo[5.4.1]dodeca-3,9-dien-12-one (**7**).



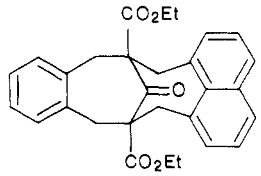
4a, R = CO_2Me; X = CO
4b, R = CO_2H; X = CO
4c, R = H; X = CO
4d, R = CO_2Me; X = CHOH
4e, R = H; X = CHOH
4f, R = H; X = CH_2
4g, R = CO_2Me; X = $CHOCH_3$



5a, R = CO_2Me; X = CO
5b, R = CO_2H; X = CO
5c, R = H; X = CO
5e, R = H; X = CHOH



6a, R = CO_2Me; X = CO
6b, R = CO_2H; X = CO
6c, R = H; X = CO
6e, R = H; X = CHOH



7

Results and Discussion

Preparation of 4, 5, 6, and 7. Compounds **4a**, **5a**, and **6a** were prepared in a one-pot method by reaction of the corresponding α,ω-dihalides with an excess of dimethyl 3-oxoglutarate (**8**) under phase-transfer conditions as summarized in Table I.

Although α,α'-dichloro-*o*-xylene did not react with **8**, reaction of the corresponding dibromo (**9a**) and diiodo derivatives (**9b**) with **8** afforded bicyclo[4.4.1]undecan-11-one **4a** in 36–60% yields. Compounds **5a** and **6a** were obtained by reaction of **8** with 2,3- (**9c**) and 1,8-bis(bro-

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[1] (a) Nogradi, M. *Stereochemistry, Basic Concepts and Application*; Pergamon Press: Oxford/New York/Toronto/Sydney/Paris/Frankfurt, 1981. (b) Dale, J. *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Ed; Wiley: New York/London/Sydney/Toronto, 1976; Vol. IX p 199. (c) Anet, F. A. L.; Anet, R. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Ed.; Academic Press: New York, 1975; Chapter 14. (d) Oki, M. *Application of Dynamic NMR Spectroscopy to Organic Chemistry* VCH Publishers: Deerfield Beach, FL, 1985.

[2] Bodennec, G.; St-Jacques, M. *Can. J. Chem.* 1977, *55*, 1199.

[3] Kamada, T. Yamamoto, O. *Chem. Lett.* 1976, 843.

[4] Kamada, T.; Yamamoto, O. *Tetrahedron Lett.* 1977, 1341.

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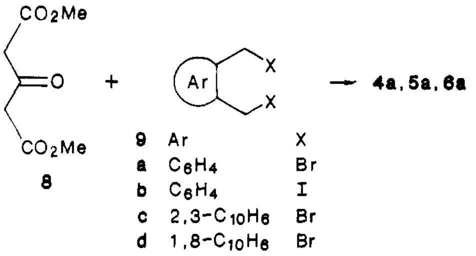
Table I. Reaction of 8 with 9

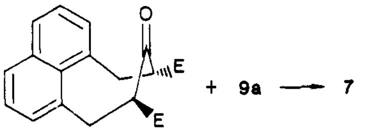


9	Ar	X
a	C_6H_4	Br
b	C_6H_4	I
c	2,3-$C_{10}H_6$	Br
d	1,8-$C_{10}H_6$	Br

9	8/9^a	cat.-base^b	product (yield, %)
9a	0.6	TBACl–NaOH	4a (36)
	1.2	TBACl–NaOH	(46)
	1.8	TBACl–NaOH	(60)
	2.3	TABCl–NaOH	(48)
	1.2	TBACl–KOH	(39)
	1.2	TBABr–NaOH	(45)
	1.2	TEBACl–NaOH	(38)
	1.2	TMAF–NaOH	(0)
9b	1.2	TBACl–NaOH	4a (24)
9c	1.8	TBACl–NaOH	5a (44)
9a	1.8	TBACl–NaOH	6a (28)

^{a}Molar ratio. ^{b}TBA, tetrabutylammonium; TEBA, benzyltriethylammonium; TMA, tetramethylammonium.

momethyl)naphthalene (**9d**). Unsymmetric **7** was prepared in 48% yield by the reaction of **3b**[4] with **9a**.



3b, E = CO_2Et

Alkaline hydrolysis of **4a**, **5a**, and **6a** afforded the corresponding dicarboxylic acids **4b**, **5b**, and **6b** in high yields. Treatment of **4b** in refluxing quinoline or *N*,*N*-dimethylaniline in the presence of copper powder resulted in only the recovery of **4b**. Decarboxylation was carried out by heating **4b** at 330 °C for 30 min and **4c** was obtained in 64% yield. Compounds **5c** and **6c** were similary prepared in 68 and 42% yields, respectively.

Reduction of **4a**, **4c**, and **5c** with $NaBH_4$ in ethanol at room temperature gave the alcohols **4d**, **4e**, and **5e** in 66, 94, and 96% yields, respectively, but **5a** was recovered unchanged under these conditions. Neither **6a** nor **6c** was reduced by $NaBH_4$ in refluxing ethanol. Reduction of **6c** was conducted with $LiAlH_4$ in dry benzene under reflux, giving **6e** in 72% yield, while reduction of **5a** under the same conditions afforded a complex mixture. Compound **4c** was reduced at the bridge carbonyl group to methylene on treatment with $LiAlH_4$–$TiCl_3$, giving **4f** in 73% yield, together with **4e** in 9% yield. Treatment of **4d** with dimethyl sulfate gave **4g** in 73% yield, while **4e** was affected by neither dimethyl sulfate nor diazomethane.

Conformational Analyses of 4–7. The ^1H and ^{13}C NMR spectra of **4a**, **4c**, **4f**, **5a**, and **5c** were temperature-dependent. The ^{13}C NMR spectrum of **4c** showed a single peak of a methylene carbon and three peaks of aromatic ring-carbons at room temperature. When the temperature was lowered to −40 °C, the signals decoalesced to indicate the existence of two kinds of methylene groups and the aromatic rings (see Table IV in Experimental Section), while the signals of the bridgehead carbons and the bridge carbonyls remained as sharp singlets.

Among the possible conformers shown in Scheme I, symmetric twin-chair (C_1) and twin-boat forms (B_1) are excluded by the NMR data. Thus **4c** exists in stereodynamic equilibrium between the two chair-boat forms, A^1 and A^{1*} at room temperature. Temperature-dependent ^{13}C NMR spectra of **4a**, **4f**, **5a**, and **5c** indicated a similar dynamic process for each of the chair-boat forms of these compounds.

Scheme I

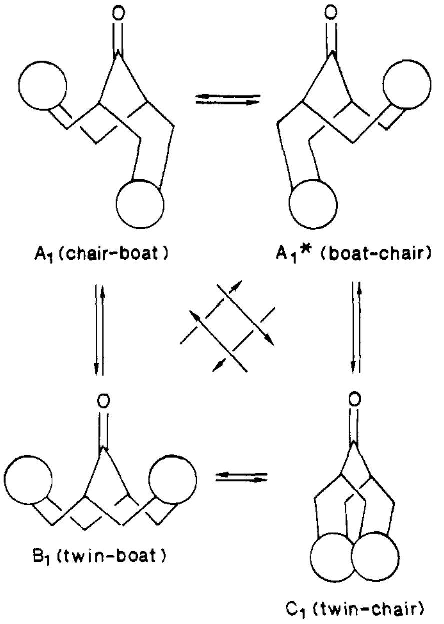


Table II. Activation Parameters of Ring Inversion^{a,b}

compd	$\Delta H^{\ddagger}$ (kcal·mol^{-1})	$\Delta S^{\ddagger}$ (eu)	$\Delta G^{\ddagger}_{298}$ (kcal·mol^{-1})
4a	14.1 ± 0.8	1.8 ± 2.7	13.6 ± 0.8
4c	12.8 ± 0.4	−0.4 ± 1.7	12.9 ± 0.4
4f	11.4 ± 0.8	5.3 ± 3.0	9.8 ± 0.8
5a	15.8 ± 1.4	1.2 ± 4.5	15.4 ± 1.4
5c	14.5 ± 0.8	−0.8 ± 2.7	14.7 ± 0.8

^{a}**4a**, **4c**, and **4f** in CD_2Cl_2. ^{b}**5a** and **5c** in $CDCl_3$.

An X-ray crystallographic study of **4a** confirmed the A_1 (or A_1*) structure.[5]

Activation parameters for the ring inversions, which were determined by dynamic ^{13}C NMR, are given in Table II.

The $\Delta G^{\ddagger}$ of the methylene-bridged **4f** is smaller than that of the carbonyl-bridged **4c** by 3 kcal mol^{-1}, the reverse of the relationship of the monocyclic analogues **1** and **2**.

The chair-to-boat conversion of **4c** and **4f** presumably proceeds by the wagging motion of the benzo group. The boat-form ring in **4c** lacks the flagpole interaction of the bridge methylene in the boat-form ring of **4f**.[6] This repulsive effect destabilizes the ground state of **4f** and is conceivably responsible for the smaller $\Delta G^{\ddagger}$ value of **4f**. Comparisons of $\Delta G^{\ddagger}$ values of **4** and **5** with those of **1** and **2** suggest that the inversion between A_1 and A_1* is a stepwise process via intermediary B_1 and/or C_1.

Dynamic NMR studies on the carboxylic acids **4b** and **5b** were difficult because of their poor solubility.

The ^{13}C NMR spectra of the alcohols **4d** and **4e** were also temperature-dependent. The spectrum of **4d** at 65 °C showed 12 sharp signals, but at 10 °C all the signals

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(5) The final atomic and the final anisotropic thermal parameters, bond lengths, bond angles, and torsion angles are available as supplementary material.

(6) Raber, D. J.; Janks C. M.; Johnston, M. D., Jr.; Raber N. K. *Tetrahedron Lett.* **1980**, *21*, 677.

(7) Tichy, M. *Advances in Organic Chemistry. Methods and Results*; Raphael, R. A., Taylor, E. C., Wynberg H., Ed.; Interscience Publishers: New York/London/Sydney, 1965; Vol. 5 p 155.

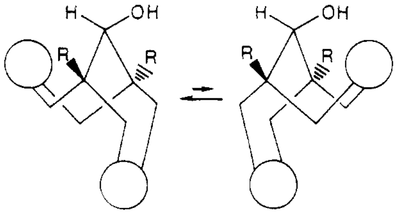
(8) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; pp 93–123.

Table III. ^{1}H NMR Spectral Data of Benzylic Protons of 4g, 6a, 6c, 6e, and 7 in CDCl$_3$

compd	δ^a	
4a	2.72 (d, J = 15)	2.36 (d, J = 15)
	3.78 (d, J = 15)	3.04 (d, J = 15)
6a	4.85 (d, J = 15)	3.71 (d, J = 15)
6c	4.70 (dd, J = 14, 12)	3.30 (dd, J = 14, 6)
6e	4.28 (dd, J = 14.5, 12)	3.33 (dd, J = 14.5, 6)
	4.05 (dd, J = 14.5, 12)	3.26 (dd, J = 14.5, 6)
7	3.76 (d, J = 15)	3.06 (d, J = 15)
	3.56 (d, J = 15)	3.19 (d, J = 15)

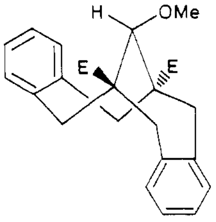
[a] Spin-coupled counterparts are on the same line. Coupling constants are in hertz.

except those of ester carbons at 52.42 and 177.76 ppm decoalesced with slight shifts in δ. The counterpart of each decoalesced signal, however, was too small to be found in the spectrum. The ^{13}C NMR signals of **4e** showed similar behavior but the signals of the decoalesced counterparts were observable (Table IV). The two chair-boat forms A$_2$ and A$_2$* of **4d** and **4e** are not equivalent. The A$_2$ form seems stereochemically more favorable than the A$_2$* form, while the latter may possibly be favored by intramolecular hydrogen bonding between the hydroxyl proton and the π-electrons of the benzene ring.[4] IR spectra of **4d** and **4e** in a CCl$_4$ solution or a KBr pellet showed a broad peak around 3400 cm^{-1} due to intermolecularly hydrogen-bonded hydroxyl groups. The broad band disappeared on dilution, with coincident appearance of a sharp peak at 3650 cm^{-1} assignable to a free hydroxyl group and a minor peak at 3600 cm^{-1} due to an intramolecularly hydrogen-bonded hydroxyl group. Thus **4d** and **4e** are considered to have primarily the A$_2$ form in dynamic equilibrium with a minor fraction of A$_2$*, which agrees well with the results of X-ray analysis of a **4d** crystal. Although a spectral study of **5e** was not carried out because of its poor solubility, **5c** might exist mainly in the A$_2$ form.



A$_2$ A$_2$*

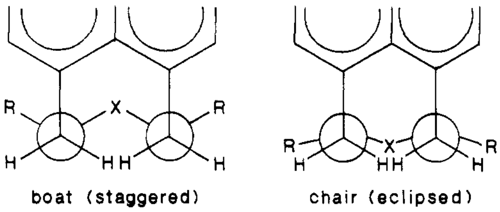
On the other hand, the ^{13}C NMR spectrum of **4g** showed no change of the signal widths in the temperature range −70 to +135 °C. The ^{1}H NMR spectrum indicated that the geminal benzylic proton signals split into two pairs of double doublets with about 1 ppm separation; those at the higher field were assigned to the two benzylic protons of the boat-form ring, which are shielded by the benzene ring annellated to the chair-form ring (Table III). Thus **4g** seems to be fixed in the A$_2$ form in this temperature range.

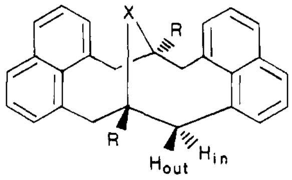


4g, E = CO$_2$Me

In contrast to bicyclo[4.4.1]undecanes **4** and **5**, the bicyclo[5.5.1]tridecanes **6a**, **6c**, and **6e** showed sharp signals in their ^{1}H NMR spectra which were invariant with temperature from −40 to +100 °C. Their ^{1}H NMR data in Table III indicate that **6a** and **6c** have a symmetrical structure and that alcohol **6e** takes a similar conformation. The vicinal coupling constants of **6c** and **6e** are in good agreement with those of the boat form of cycloocta[*d*,*e*]naphthalen-9-one **3**.[3,4] Furthermore, the IR spectrum of **6e** measured on a KBr pellet showed a single sharp ν_{OH} band at 3600 cm^{-1}, indicating the absence of an intermolecular hydrogen bond in the solid phase. This result contrasts with that of **4e** in the unsymmetrical chair-boat form. Thus it is concluded that **6a**, **6c**, and **6e** are fixed in a symmetrical twin-boat form.

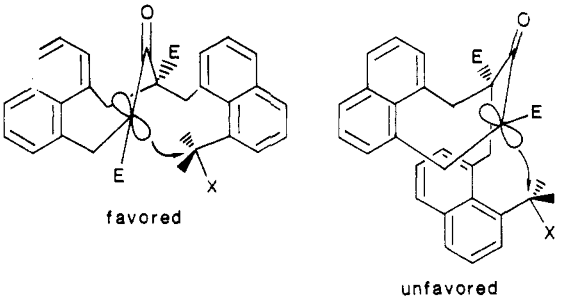
Chart I. Newman Projection of Staggered and Eclipsed Conformation in 6





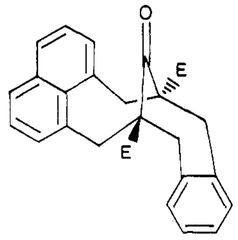
6

The boat form of **6** has a favorable staggered conformation at the bond between the bridgehead and benzylic carbons, while the corresponding C–C bonds of the chair form is compelled to take an unfavorable eclipsed conformation (Chart I). This conformational barrier, however, seems to be not high enough for **6** to be fixed in the twin-boat form in the temperature range examined. Studies of molecular models reveal that the bicyclic ring of **6** is so rigid that it is difficult to convert from boat to chair and vice versa. It is reasonable, therefore, to consider that the stereochemistry of the twin-boat form of **6** is determined by the conformation of its monocyclic precursor during nucleophilic ring closure and cannot invert even under the influence of the flagpole repulsion in **6e** after the bicyclic system is formed.



E = CO$_2$Me, X = Br

Finally, the stereochemistry of a composite system of the 1,2-benzo seven-membered ring and the 1,8-naphtho eight-membered ring, the bicyclo[5.4.1]dodecan-12-one **7**, was examined. Compound **7** showed a temperature-independent ^{13}C NMR sepctrum in the range −50 to +50 °C. The ^{1}H NMR spectrum of **7** (Table III) showed two pairs of double doublets assignable to benzylic protons. The δ values of both pairs are 1 ppm higher than those of the corresponding signals of the di(1,8-naphtho)bicyclic **6a** and similar to those of the chair-form ring of the di(benzo)-bicyclic **4g**. The chemical shifts and spin-coupling patterns may be rationalized by considering that the eight-membered ring of **7** takes a boat form with its methylene protons shielded by the benzene ring annellated to the seven-membered chair-form ring and that the chair-boat conformation is fixed in the above temperature range.



7, E = CO_2Et

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 on KBr pellets. ^{13}C and ^1H NMR (internal Me_4Si) spectra were taken on a Nippon Denshi JEOL FX-100 NMR spectrometer. Mass spectra were recorded on a Nippon Denshi JMS-O1SG-2 mass spectrometer at 75 eV using a direct-inlet system.

Dimethyl 11-Oxodibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylate (4a). A mixture of **8** (4.50 g) in CH_2Cl_2 (20 mL) was added dropwise at room temperature to a vigorously stirred mixture of **9a** (3.90 g) and TBACl (2.40 g) in CH_2Cl_2 (40 mL) and 25% aqueous NaOH solution (20 mL) over a period of 45 min. The reaction mixture was stirred for 1 h. The organic layer was separated, dried (Na_2SO_4), and evaporated in vacuo to leave a residue which, on trituration with ethanol, gave a colorless solid. Recrystalization of the solid from ethanol afforded 1.67 g (60%) of **4a** as colorless prisms: mp 183–184 °C; IR 1745, 1690 cm^{-1}; mass spectrum, *m/e* 378 (M^+), 360, 269, 104. Anal. Calcd for $C_{23}H_{22}O_5$: C, 73.00; H, 5.86. Found: C, 73.11; H, 5.96.

Dimethyl 11-Oxodinaphtho[2,3-*c*;2′,3′-*h*]bicyclo[4.4.1]-undeca-3,8-diene-1,6-dicarboxylate (5a). A mixture of **9c** (1.50 g) and TBACl (0.80 g) in CH_2Cl_2 (20 mL) and 25% aqueous NaOH solution (10 mL) was treated with a mixture of **8** (1.50 g) in CH_2Cl_2 (15 mL) as described above to afford 0.50 g (44%) of **5a**: colorless prisms (ethanol); mp 300–301 °C; IR 1730, 1690 cm^{-1}; mass spectrum, *m/e* 478 (M^+), 460, 369, 165, 154. Anal. Calcd for $C_{31}H_{26}O_5$: C, 77.81; H, 5.48. Found: C, 77.92; H, 5.43.

Dimethyl 13-Oxodinaphtho[1,8a,8-*cd*;1′,8a′,8′-*ij*]bicyclo-[5.5.1]trideca-3,9-diene-1,7-dicarboxylate (6a). A mixture of **9d** (8.18 g) and TBACl (4.90 g) in CH_2Cl_2 and 25% aqueous NaOH solution (53 mL) was treated with a mixture of **8** (8.00 g) in CH_2Cl_2 (80 mL) as described above to give 1.65 g (28%) of **6a**: colorless prisms (ethanol); mp 313–315 °C; IR 1740, 1720, 1690 cm^{-1}; mass spectrum, *m/e* 478 (M^+), 165, 153; ^1H NMR 3.28 (s, 6 H), 7.16–7.32 (m, 8 H), 7.60–7.79 (m, 4 H). Anal. Calcd for $C_{31}H_{26}O_5$: C, 77.81; H, 5.48. Found: C, 77.76; H, 5.45.

Diethyl 12-Oxonaphtho[1,8a,8-*cd*]benzo[*i*]bicyclo[5.4.1]-dodeca-3,9-diene-1,7-dicarboxylate (7). To a vigorously stirred mixture of **9a** (1.00 g) and TBACl (0.60 g) in CH_2Cl_2 (20 mL) and 23% aqueous NaOH solution (8 mL) was added dropwise a solution of **3b** (1.24 g) in CH_2Cl_2 (20 mL) at room temperature. After the mixture was stirred at room temperature for 4 h, the organic layer was separated, washed with water, dried over Na_2SO_4, and evaporated in vacuo to leave **7** which was recrystallized from benzene to give 0.82 g (48%) of colorless prisms: mp 188–191 °C; IR 1735, 1685 cm^{-1}; mass spectrum, *m/e* 456 (M^+), 165, 153; ^1H NMR 1.14 (t, *J* = 7 Hz, 6 H), 3.06 (d, *J* = 15 Hz, 2 H), 3.19 (d, *J* = 15 Hz, 2 H), 3.76 (d, *J* = 15 Hz, 2 H), 4.12 (q, *J* = 7 Hz, 4 H), 7.10–7.36 (m, 6 H), 7.42–7.68 (m, 4 H) ppm. Anal. Calcd for $C_{29}H_{28}O_5$: C, 76.30; H, 6.18. Found: C, 76.11; H, 6.18.

11-Oxodibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylic Acid (4b). A mixture of **4a** (1.00 g) and KOH (3.50 g) in ethanol (30 mL) was refluxed for 2 h. The reaction mixture was poured into water (150 mL) and acidified with concentrated hydrochloric acid. The precipitated white solid was collected by filtration and recrystallized from ethanol to give colorless prisms of **4b** (0.89 g, 96%): mp 308 °C dec; IR 3400–2600, 1700 cm^{-1}; mass spectrum, *m/e* 350 (M^+), 288, 270, 104. Anal. Calcd for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 71.81; H, 5.33.

11-Oxodinaphtho[2,3-*c*;2′3′-*h*]bicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylic Acid (5b). A mixture of **5a** (0.18 g) and KOH (0.50 g) in ethanol (8 mL) was treated as described above to give colorless prisms (AcOH) of **5b** (0.16 g, 94%): mp 320 °C dec; IR 3500–2700, 1720 cm^{-1}; mass spectrum, *m/e* 450 (M^+), 406, 388, 233, 155, 154. Anal. Calcd for $C_{29}H_{22}O_5$: C, 77.32; H, 4.92. Found: C, 77.05; H, 4.88.

13-Oxodinaphtho[1,8a,8-*cd*;1′,8a′,8′-*ij*]bicyclo[5.5.1]trideca-3,4-diene-1,7-dicarboxylic Acid (6b). A mixture of **6a** (1.00 g) and KOH (6.00 g) in ethanol (50 mL) was treated as described above to give colorless prisms (ethanol) of **6b** (0.89 g, 95%): mp 360 °C dec; IR 3300–2600, 1720, 1680 cm^{-1}; mass spectrum, *m/e* 450 (M^+), 406, 362, 165, 153. Anal. Calcd for $C_{29}H_{22}O_5$: C, 77.32; H, 4.98. Found: C, 77.33; H, 4.98.

Dibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one (4c). Compound **4b** (2.00 g) was heated at 330 °C for 30 min and the residue was recrystallized from benzene to give colorless prisms of **4c** (0.96 g, 64%): mp 132–135 °C; IR 1700 cm^{-1}; mass spectrum, *m/e* 262 (M^+), 157. Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 86.74; H, 6.92.

Dinaphtho[2,3-*c*;2′,3′-*h*]bicyclo[4.4.1]undeca-3,8-dien-11-one (5c). Compound **5b** (1.90 g) was pyrolyzed at 360 °C for 30 min to yield **5c** (1.03 g, 68%) as colorless prisms (benzene): mp 293–294 °C; IR 1700 cm^{-1}; mass spectrum, *m/e* 362 (M^+), 207, 77. Anal. Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.49; H, 6.11.

Dinaphtho[1,8a,8c-*cd*;1′,8a′,8′-*ij*]bicyclo[5.5.1]trideca-3,9-dien-13-one (6c). Compound **6b** (1.40 g) was pyrolyzed at 400 °C for 30 min to give **6c** (0.47 g, 42%) as colorless prisms (benzene): mp 410 °C dec; IR 1700 cm^{-1}; mass spectrum, *m/e* 362 (M^+), 165, 153; ^1H NMR 2.60–3.10 (m, 2 H), 7.24–7.42 (m, 8 H), 7.60–7.80 (m, 4 H) ppm. Anal. Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.24; H, 6.05.

Dimethyl 11-Hydroxydibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylate (4d). A mixture of **4a** (0.30 g) and $NaBH_4$ (0.15 g) in ethanol (30 mL) was stirred at room temperature for 7 h and poured into 0.5 N hydrochloric acid (50 mL). The precipitated solid was collected by filtration and recrystallized from ethanol to give **4d** (0.20 g, 66%): colorless prisms; mp 216–218 °C; IR 3460, 1720 cm^{-1}; mass spectrum, *m/e* 380 (M^+), 330, 302, 271, 243, 104. Anal. Calcd for $C_{23}H_{24}O_5$: C, 72.61; H, 6.35. Found: C, 72.74; H, 6.46.

11-Hydroxydibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-diene (4e). A mixture of **4c** (1.00 g) and $NaBH_4$ (0.58 g) in ethanol (40 mL) was treated as described above to yield **4e** (0.95 g, 94%: colorless needles (ethanol); mp 163–164 °C; IR 3350 cm^{-1}; mass spectrum, *m/e* 264 (M^+), 141, 129, 104. Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.42; H, 7.79.

11-Hydroxynaphtho[2,3-*c*;2′,3′-*h*]bicyclo[4.4.1]undeca-3,8-diene (5e). A mixture of **5c** (0.50 g) and $NaBH_4$ (0.20 g) in ethanol (40 mL) was stirred at room temperature for 21 h and treated as described above to give **5e** (0.48 g, 96%): colorless needles (benzene); mp 330–332 °C; IR 3350 cm^{-1}; mass spectrum, *m/e* 364 (M^+), 191, 179. Anal. Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 89.03; H, 6.65.

13-Hydroxydinaphtho[1,8a,8-*cd*;1′,8a′,8′-*ij*]bicyclo[5.5.1]-trideca-3,9-diene (6e). After a mixture of **6c** (0.30 g) and $LiAlH_4$ (0.20 g) in anhydrous benzene (50 mL) was stirred at reflux for 20 h, it was poured into 2% aqueous hydrochloric acid (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (60 mL). The extract was combined with the organic layer, washed with water (10 mL), and dried over Na_2SO_4. Evaporation of the solvent in vacuo afforded a white solid which, on recrystallization from benzene, yielded **6e** (0.146 g, 72%): colorless prisms; mp 287–290 °C; IR 3300 cm^{-1}; mass spectrum, *m/e* 364 (M^+), 179, 165, 153; ^1H NMR 0.80–1.60 (br, 1 H), 2.30–3.05 (m, 2 H), 4.04 (m, 1 H), 7.10–7.50 (m, 8 H), 7.54–7.82 (m, 4 H) ppm. Anal. Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 88.91; H, 6.75.

Dibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-diene (4f). A mixture of $LiAlH_4$ (0.30 g) and $TiCl_3$ (2.40 g) in anhydrous THF (20 mL)

Table IV. Decoalesced ^{13}C NMR Chemical Shifts of the Bicyclic Systems (in ppm from Me_4Si in $CDCl_3$)

compd	temp, °C	benzylic methylene	bridge head	bridge carbon	aromatic ring carbons (mult at off-resonance[a])	ester carbon	ester alkyl
4a	0	35.75, 40.13	64.24	207.22	127.19 (D), 128.47 (D), 130.75 (D), 132.39 (D), 136.78 (S), 137.83 (S)	173.17	52.65
4c	−40	32.47, 37.44	53.41	215.70	127.19 (D), 127.54 (D), 128.94 (D), 132.22 (D), 138.18 (S), 138.89 (S)		
4d	22	35.28, 36.74	48.79	73.08	126.89 (D), 127.07 (D), 128.94 (D), 132.10 (D), 135.96 (S), 137.77 (S)	177.76	52.42
4e	−50	33.11, 33.64 36.56, 39.90	71.67	*b*	126.13 (D), 126.37 (D), 128.06 (D), 131.51 (D), 138.24 (S), 139.82 (S)		
4f	−50	34.98, 42.65	30.71	38.38	126.02 (D), 128.00 (D), 131.75 (D), 139.70 (S), 140.17 (S)		
4g	−70	35.04, 36.86	47.91	51.87 84.65[c]	126.78 (D), 127.01 (D), 129.47 (D), 132.04 (D), 136.37 (S), 138.30 (S)	176.62	59.73
5a	20	35.75, 40.19	64.24	206.00	125.43, 126.49, 127.25. 129.12, 130.88, 132.63, 132.98, 134.27, 134.97	172.82	52.42
5c	−30	32.47, 37.56	53.47	216.23	125.37, 126.02, 127.01, 127.19, 128.24, 130.52, 132.33, 135.61, 136.37		
6a	25	46.10	68.27	202.40	124.79 (D), 129.76 (D), 131.69 (D), 131.98 (S), 132.75 (S), 135.32 (S)	171.54	51.48
7	−50	39.37, 41.42	63.48	205.70	124.08 (D), 128.00 (D), 129.70 (D), 131.05 (D), 131.28 (S), 131.98 (S), 133.33 (D), 134.50 (S), 135.90 (S)	171.92	13.92 61.31

[a] (S) singlet, (D) doublet. [b] Overlapped in $CDCl_3$ signals. [c] OCH_3 on the bridge carbon.

was heated at reflux for 1 h. To the mixture was added dropwise a solution of **4c** (0.74 g) in anhydrous THF (10 mL), and the mixture was heated at reflux for 22 h. To it was added a 20% aqueous K_2CO_3 solution (100 mL), and it was filtered. The filtrate was extracted with THF (20 mL × 3) and the extract was washed with water, dried over Na_2SO_4, and evaporated in vacuo to leave a solid which was triturated with hexane and filtered to give **4e** (0.07 g, 9%). The filtrate was evaporated and the residue was recrystallized from methanol to give colorless needles of **4f** (0.51 g, 73%): mp 110–112 °C; mass spectrum, *m/e* 248 (M^+), 143, 128. Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.77; H, 8.11.

Dimethyl 11-Methoxydibenzo[*c*,*h*]bicyclo[4.4.1]undeca-3,8-diene-1,6-dicarboxylate (4g). After a mixture of **4d** (2.00 g) and TBAI (0.20 g) in CH_2Cl_2 (20 mL) and 50% aqueous NaOH solution (6 mL) was vigorously stirred at room temperature for 30 min, dimethyl sulfate (1 mL) was added, and the mixture was stirred for 3 h. Concentrated aqueous ammonia was added, and stirring was continued for 30 min. It was poured into water (50 mL) and the organic layer was separated, washed with water, dried over Na_2SO_4, and evaporated in vacuo to leave a residue which, on recrystallization from ethanol, afforded **4g** (1.51 g, 73%): colorless prisms; mp 182–185 °C; IR 1720 cm^{-1}; mass spectrum, *m/e* 394 (M^+), 330, 302, 271, 243; ^{1}H NMR 2.36, 2.72, 3.04, and 3.78 (each d, J = 15 Hz, 2 H), 3.10 (s, 3 H), 3.70 (s, 6 H), 3.90 (s, 1 H), 6.88–7.20 (m, 8 H) ppm. Anal. Calcd for $C_{24}H_{26}O_5$: C, 73.08; H, 6.64. Found: C, 72.85; H, 6.61.

Dynamic NMR Spectroscopy. Kinetic data on the ring inversions of **4a**, **4c**, **4f**, **5a**, and **5c** were measured by dynamic ^{13}C NMR in the temperature range 0–30 °C (data number, n = 15), −40 to 20 °C (n = 10), −50 to 50 °C (n = 17), −20 to 60 °C (n = 24), and −10 to 50 °C (n = 15). Rate constants K were calculated by approximate methods by use of the signal widths and the separations of decoalesced signals, and the activation parameters were obtained from Eyring plots.[7] Error ranges are described in terms of standard deviation.

Decoalesced ^{13}C NMR data of **4a**, **4c**, **4d**, **4e**, **4f**, **4g**, **5a**, and **5c** are given in Table IV, together with ^{13}C NMR chemical shifts of rigid systems **6a** and **7**.

X-ray Analyses. (a) Single crystals of **4a** were prepared by recrystallization from ethanol. They were monoclinic, space group $P12_1/a1$, with a = 10.767 (16) Å, b = 12.435 (2) Å, c = 13.930 (3) Å, and d_{calcd} = 1.349 g·cm^{-3} for Z = 4 (M_r 378.41). The intensity data were measured on a CAD4 diffractometer (Mo K radiation, monochromated, ω–2θ scans). The size of the crystal used for data collection was approximately 0.6 × 0.3 × 0.2 mm. No absorption correction was necessary (μ = 0.884). A total of 3278 independent reflections were measured for $\theta \le 25°$, of which 1999 were considered to be observed [$I \geq 3.0\theta\ (I)$]. The structure was solved by direct methods by using MULTAN 82 and refined by fullmatrix for non-hydrogen atoms. The final discrepancy indices were R = 0.041 and R_w = 0.045 for the 1999 observed reflections. No peaks greater than ±0.2 eA^{-3} were found in the difference Fourier map.

(b) Single crystals of **4d** were prepared by recrystallization from ethanol. They were monoclinic, space group $P112/b$, with a = 9.051 (3) Å, b = 9.928 (4) Å, c = 23.90 (2) Å, with d_{calcd} = 1.20 g·cm^{-3} for Z = 4 (M_r 380.42). The procedure used was the same as in the preceding paragraph with a crystal of approximately 0.7 × 0.7 × 0.5 mm, no absorption correction was used (μ = 0.863), and 4712 reflections were measured of which 3651 were considered to be observed. The final discrepancy indices were R = 0.057 and R_w = 0.056 for the 3651 observed reflections. In the final difference Fourier map, two peaks of 0.31 and 0.30 eA^{-3}, respectively, were found close to the methyl groups of ester linkages. The other difference Fourier peaks were smaller than 0.3 eA^{-3}.

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Registry No. **3b**, 61322-96-1; **4a**, 104663-70-9; **4b**, 104663-71-0; **4c**, 99030-04-3; **4d**, 104663-72-1; **4e**, 104663-73-2; **4f**, 104663-74-3; **4g**, 104663-75-4; **5a**, 104663-76-5; **5b**, 104663-77-6; **5c**, 104663-78-7; **5e**, 104663-79-8; **6a**, 104663-80-1; **6b**, 104663-81-2; **6c**, 104663-82-3; **6e**, 104663-83-4; **7**, 104663-84-5; **8**, 1830-54-2; **9a**, 91-13-4; **9c**, 38998-33-3; **9d**, 2025-95-8.

Supplementary Material Available: Crystal data, positional and thermal parameters, bond distances and angles, torsional angles as well as ORTEP drawings for **4a** and **4d** (18 pages); structure factor tables for **4a** and **4d** (31 pages). Ordering information is given on any current masthead page.