m/z 245 (M^+, 66), 200 [$(M - OEt)^+$, 100], and 188 (52.6). Anal. Calcd for $C_{14}H_{15}NO_3$; C, 68.56; H, 6.16; N, 5.71. Found: C, 68.49; H, 6.20; N, 5.59.

3,4-Furo-2-quinolone **37** (47 mg, 55%) was also obtained when isomeric adduct **30** (86 mg, 0.35 mmol) in benzene (10 mL) containing mercury(II) oxide (226 mg, 1.04 mmol) and iodine (265 mg, 1.04 mmol) was irradiated for 3 h.

(f) Cyclobutanol 34. Irradiation of cyclobutanol **34** (100 mg, 0.41 mol) in benzene (20 mL) containing mercury(II) oxide (263 mg, 1.22 mmol) and iodine (307 mg, 1.22 mmol) for 2 h as above gave furoquinolone **38** (50 mg, 50%): R_f 0.27 (1:1 ethyl acetate–hexane); mp 69–72 °C (diethyl ether–hexane); IR (thin film) 1650 and 1638 cm^{-1} (lactam C=O); ^1H NMR (90 MHz) δ 1.76 (3 H, s, Me), 3.07 and 3.20 (each 1 H, each d, J = 16.7 Hz, 3-H), 3.35 (3 H, s, OMe), 3.71 (3 H, s, NMe), and 7.1–8.1 (4 H, m, aromatic H); MS, *m/z* 245 (M^+, 66) and 200 [$(M - OEt)^+$, 100]; high-resolution mass spectrum for $C_{14}H_{15}NO_3$ calcd 245.1051, found 245.1045.

(g) Cyclobutanol 41. Irradiation of cyclobutanol **41** (210 mg, 0.76 mmol) in benzene (35 mL) containing mercury(II) oxide (494 mg, 2.28 mmol) and iodine (579 mg, 2.28 mmol) for 2.5 h and workup as above gave a mixture of products, which was subjected to preparative TLC to give furoquinolines **45** (84 mg, 40%) and **46** (43 mg, 21%) in order of their mobility. **Photoproduct 45**: R_f 0.17 (1:1 ethyl acetate–hexane); mp 179–181 °C (hexane–dichloromethane–methanol); IR (Nujol) 1745 (OAc), 1671 and 1639 cm^{-1} (lactam C=O); ^1H NMR (90 MHz) δ 1.97 and 2.06 (each 3 H, each s, OAc and Me), 3.24 and 3.60 (each 1 H, each d, J = 17.15, 3-H), 3.70 (3 H, s, NMe), 7.2–7.7 (4 H, m, aromatic H); MS, *m/z* 273 (M^+, 5.2), 213 [$(M - CH_3COOH)^+$, 100], 189 (92.6), and 188 (84.3). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.53; N, 5.13. Found: C, 65.66: H, 5.41; N, 5.24.

Photoproduct 46: R_f 0.08 (1:1 ethyl acetate–hexane); mp 180 °C (diethyl ether–hexane–dichloromethane); IR (Nujol) 1739 (OAc), 1639 and 1588 cm^{-1} (enone C=O); ^1H NMR (90 MHz) δ 2.07 and 1.97 (each 3 H, each s, OAc and Me), 3.28 and 3.61 (each 1 H, each d, J = 15.8, 3-H), 3.70 (3 H, s, NMe), 7.3–7.7 (3 H, m, aromatic H), and 8.45 (1 H, d, J = 7.91, aromatic H); MS, *m/z* 273 (M^+, 10.5), 213 [$(M - AcOH)^+$, 42], and 188 (100). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.53; N, 5.13. Found: C, 65.66; H, 5.42; N, 5.21.

(h) Cyclobutanol 44. Irradiation of cyclobutanol **44** (255 mg, 0.79 mmol) in benzene (30 mL) containing mercury(II) oxide (513 mg, 2.37 mmol) and iodine (602 mg, 2.37 mmol) for 4.5 h and workup as above gave furoquinolones **47** (42 mg, 17%) and **48** (78 mg, 31%) in order of their mobility. **47**: R_f 0.26 (1:1 ethyl acetate–hexane); mp 182–183 °C (diethyl ether–hexane–methanol): IR (thin film) 1730 ($OCOC_6H_5$), 1664 and 1639 cm^{-1} (lactam C=O); ^1H NMR (270 MHz) δ 3.40 (1 H, dd, J = 17.22 and 2.20 Hz, 3-H), 3.63 (1 H, dd, J = 17.22 and 7.33 Hz, 3-H), 3.75 (3 H, s, NMe), 7.2–7.3 (2 H, m, aromatic H), 7.4–7.5 (3 H, m, aromatic H), 7.55–7.65 (2 H, m, aromatic H), 7.82 (1 H, dd, J = 1.47 and 7.70 Hz, 9-H), and 8.06 [2 H, dd, J = 1.10 and 7.32 Hz, benzoyl H(ortho)]; MS, *m/z* 321 (M^+, 0.6), 293 (3.7), 199 [$(M - C_6H_5COOH)^+$, 51], and 105 (100); high-resolution mass spectrum for $C_{19}H_{19}NO_4$ calcd 321.1000, found 321.0984. **48**: R_f 0.06 (1:1 ethyl acetate–hexane); mp 211 °C (diethyl ether–hexane–dichloromethane); IR (thin film) 1732 ($OCOC_6H_5$), 1630 and 1592 cm^{-1} (enone C=O); ^1H NMR (270 MHz) δ 3.47 (1 H, dd, J = 16.12 and 2.19 Hz, 3-H), 3.66 (1 H, dd, J = 16.12 and 6.96 Hz, 3-H), 3.73 (3 H, s, NMe), 7.89 (1 H, dd, J = 6.96 and 2.19 Hz, 1-H), 7.35–7.5 (3 H, m, aromatic H), 7.55–7.7 (2 H, m, aromatic H), 8.07 [2 H, dd, J = 8.43 and 1.19 Hz, benzoyl H_2 (ortho)], and 8.50 (1 H, dd, J = 7.69 and 1.46 Hz, 5-H); MS, *m/z* 321 (M^+, 1.7), 199 [$(M - C_6H_5COOH)^+$, 18], and 105 (100); high-resolution mass spectrum for $C_{19}H_{15}NO_4$ calcd 321.1000, found 321.0990. Similar irradiation of **43** (198 mg, 0.61 mmol) in benzene (31 mL) containing mercury(II) oxide (396 mg, 1.83 mmol) and iodine (464 mg, 1.83 mmol) for 5 h gave **47** (42 mg, 22%) and **48** (79 mg, 40%).

Supplementary Material Available: Anisotropic thermal parameters for the non-hydrogen atoms (Table II), fractional atomic coordinates, (Table III), bond distances and angles for compound **16** (Table IV), and perspective view of the molecule (Figure II) (4 pages). Ordering information is given on any current masthead page.

Static and Dynamic Stereochemistry of a Chiral, Doubly Bridged 9,10-Diphenylanthracene from a Stereospecific Polycyclic Aromatic Dicarbonyl Coupling

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The reductive coupling of dibenzo[*b,f*]suberone (**5**) with a low-valent titanium reagent generated from $TiCl_4$, Zn, and pyridine in THF gave two dimeric hydrocarbons, the tetrahydrobis(benzocyclohept)anthracene **6** and the tetrahydrobi(dibenzocycloheptenyl) **7**. The same reaction with reagents generated from $TiCl_3$ or $TiCl_4$ with $LiAlH_4$ in THF gave only **7**. Analogous couplings of dibenzo[*b,f*]tropone (**4**) gave bi(dibenzo[*a,d*]cycloheptenyl) (**9**) and *syn*-bis(dibenzo[*a,d*]cycloheptenylidene) (**3**). X-ray cryystallography showed **6** to be a chiral, syn-bridged 9,10-diphenylanthracene. Molecular mechanics calculations (MM2-85) predicted a very similar syn-bridged structure to be the lowest energy conformation and a centrosymmetric anti form to be 1.39 kcal/mol higher in energy. **6** could be resolved into enantiomers by chromatography at 5 °C on swollen, microcrystalline triacetylcellulose with ethanol as eluent. Analysis of the CD spectrum in terms of the coupled oscillator model led to the assignment of (−)-**6** to the *S,S* configuration. Thermal racemization, monitored by the CD spectrum, in the temperature range 20–50 °C gave $\Delta G^{\ddagger}$ = 22.6 kcal/mol for the ring inversion. Analysis of the ^1H NMR spectrum showed the conformations of the CH_2–CH_2 bridges in solution to be similar to those in the crystal, and simulation of the exchange-broadened spectra in the temperature range 144–169 °C gave $\Delta G^{\ddagger}_{inv}$ = 22.9 kcal/mol. No resonances due to an anti form could be observed in the NMR spectra.

The bistricyclic ethylene (**1**; Chart I) enigma has fascinated chemists since thermochromism and photochromism were revealed in bianthrones (**1**, X = C=O).[1,2] The bistricyclic ethylenes are attractive substrates for the study

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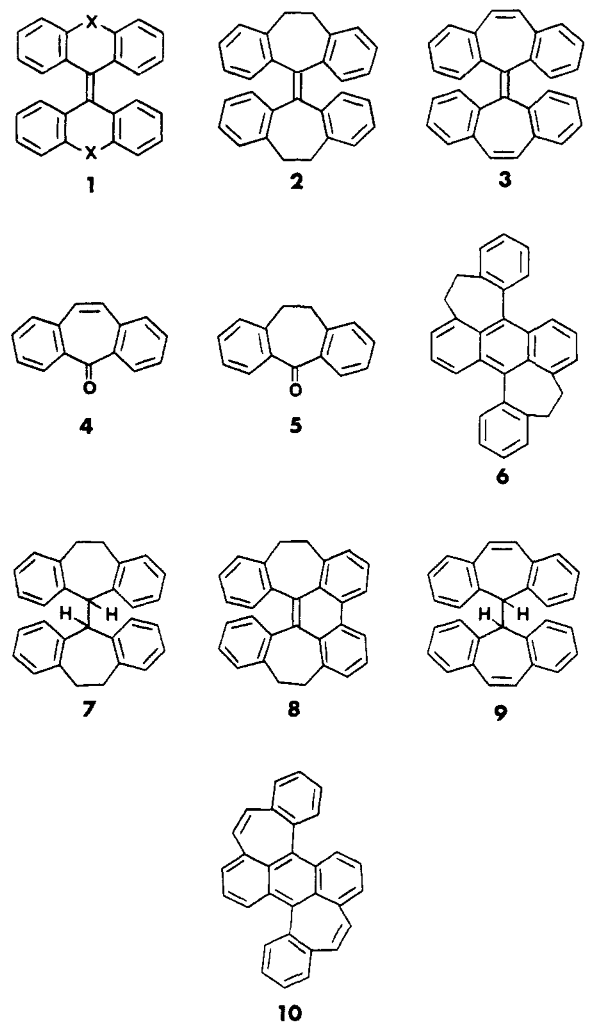
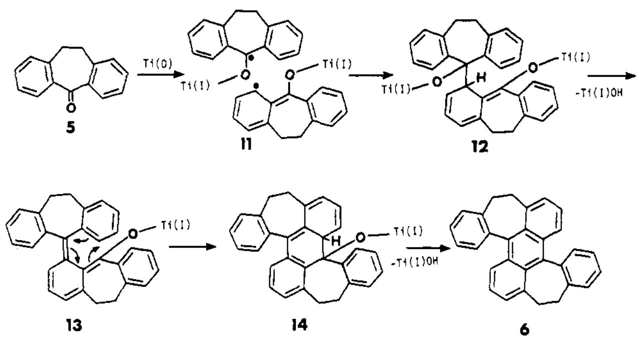
Chart I



Scheme I



of the ground-state conformation and the dynamic behavior of overcrowded ethylenes.[3-5] Intramolecular overcrowding is a steric effect shown by aromatic structures *in which the (intramolecular) distance of the closest approach between nonbonded atoms, calculated on the basis of conventional bond lengths and bond angles, is smaller than the sum of the van der Waals radii of the involved atoms*.[4-6] An idealized coplanar bistricyclic ethylene would maintain very short nonbonded carbon–carbon and hydrogen–hydrogen distances, e.g., C1–C1′ and H1–H1′ in **1**), leading to a considerable overlap of the van deer Waals radii in the region of the central carbon–carbon double bond (C9═C9′). The associated repulsive interactions could, in principle, be alleviated by deviation from coplanarity and by various distortions. Studies of the static and dynamic stereochemistry of disubstituted **1** with six-membered central rings (**1**, X = CO, O, NCH$_3$) have shown that these overcrowded ethylenes undergo fast thermal *E,Z* isomerizations ($\Delta G^{\ddagger} \approx 17$–$22$ kcal/mol).[7] This unusual behavior was attributed predominantly to the ground-state destabilization due to steric strain in the anti-folded conformation of **1**.[7] The effect is expected to be diminished in analogous systems with seven-membered central rings, e.g., **2** (**1**, X = CH$_2$—CH$_2$) and **3** (**1**, X = CH═CH), in which the overcrowding is less pronounced due to larger flexibility of the central rings. Syntheses of unsubstituted **2** and **3** have previously been reported,[8,9] and ambiguities in the early syntheses[10,11] have been resolved.[8,9,12] Two stable stereoisomers of **3** have been isolated and characterized: *syn*-**3** and *anti*-**3**.[8,9,12] In the case of **2**, only the anti-folded isomer is known.[9,13] The crystal and molecular structures of *anti*-**2**, *syn*-**3**, and *anti*-**3** have been described.[5,13,14] Syn and anti refer to the direction of folding of the benzene rings in the two tricyclic units. Folding is manifested by a symmetrical deviation from planarity of the tricyclic unit, namely the out-of-plane bending of the two peripheral benzene rings from the center of the tricyclic system and its least-squares plane.

A direct synthesis of **2** and **3**, which could be extended to tailor-made derivatives with appropriate substitution patterns, was required. The titanium-induced dicarbonyl coupling reaction[15] of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**4**) and of its 10,11-dihydro derivative **5** seemed a promising, one-flask entry into the series of **2** and **3**. We report below the results of these dicarbonyl coupling reactions. Special emphasis is given to the titanium-induced aromatization coupling of **5** leading to 8,9,17,18-tetrahydrobis(benzo[4,5]cyclohept)[1,2,3-*de*:1′,2′,3′-*kl*]anthracene (**6**), a chiral strained PAH (Scheme I).[16] We describe here the synthesis, crystal and molecular structure, molecular mechanics calculations, and dynamic NMR studies of **6** as

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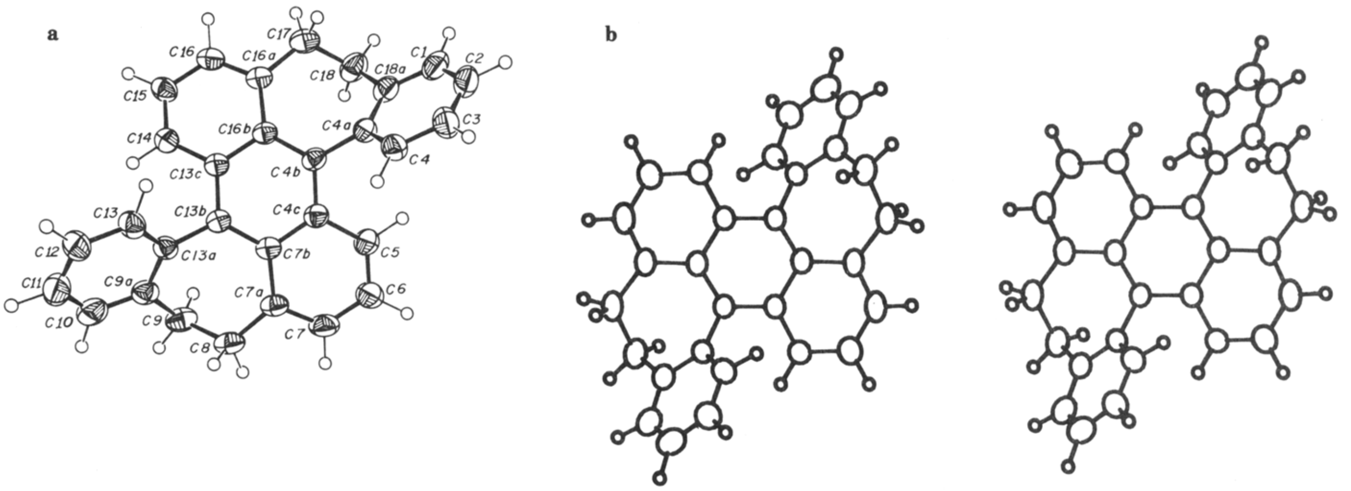

Figure 1. (a) ORTEP drawing of (*R*,*R*)-(**6**). (b) Stereoscopic view of the anti form of **6**.

well as resolution, determination of the absolute configuration, electronic and CD spectra, and kinetics of the racemization of (−)-**6**. Finally, we propose a mechanism for the (−)-**6** ⇌ (+)-**6** enantiomerization.

The reductive coupling of **5** with a low-valent titanium reagent generated from $TiCl_4$ and $LiAlH_4$ in THF gave only 10,10′,11,11′-tetrahydro-5,5′-bis(5*H*-dibenzo[*a*,*d*]-cycloheptenyl) (**7**)[17,18] in 69% yield, and *none of* **2**. Starting from $TiCl_3$ and $LiAlH_4$, the reductive coupling of **5** in THF gave **7** in 63% yield, without any **2**. Under the Mukaiyama–Lenoir variation of the McMurry reaction,[19,20] treatment of **5** with a low-valent titanium reagent generated from $TiCl_4$, Zn, and pyridine in THF gave a mixture of dimeric products, but again none of **2**. Column chromatography afforded two major products, the dimeric colorless hydrocarbon ($C_{30}H_{24}$) **7** in 33% yield and a $C_{30}H_{22}$ hydrocarbon (m/e 382, M^+, 100%). Purification of the latter by sublimation gave **6** as red crystals in 26% yield, with 15 distinct ^{13}C NMR signals, consistent with C_2 symmetry. The absence of aromatic signals below δ 8.0 ruled out the structure of 7,8,17,18-tetrahydrobis(benzo-[4,5]cyclohepta)[1,2,3-*jk*:3′,2′,1′-*nm*]phenanthrene (**8**), which could have been formed by oxidative aromatization of **2**.

The structure of **6**, which is a homologue of rubicene,[21] was eventually determined by X-ray crystallography (vide infra). Two additional products were separated from the reaction mixture: an unidentified yellow fluorescent compound which, according to the mass spectrum at 300 °C, may be a tetramer (m/e 764–768, $C_{60}H_{44-48}$?) and (pyridine)$_2ZnCl_2$.[22]

The analogous reductive coupling of **4** with a low-valent titanium reagent generated from $TiCl_4$, Zn, and pyridine in THF afforded the following dimeric products: 5,5′-bi(5*H*-dibenzo[*a*,*d*]cycloheptenyl) (**9**)[9,23] in 45% yield and *syn*-**3**[9] in 11% yield, but none of *anti*-**3**[8,9] or of **10** (the analogue of **6**). A trimeric product was also formed but was not characterized. Its mass spectrum at 220 °C showed the ion of highest mass at m/e 587 ($C_{45}H_{31}O$?) and the strongest signals at m/e 395 and 396 ($C_{30}H_{20}O$?). When the coupling was carried out under the conditions of the McMurry procedure[15] ($TiCl_3/LiAlH_4$ in THF), a 58% yield of **9** was obtained, but none of *syn*-**3**, *anti*-**3**, or **10**.

Table I. Crystal Data for 6

formula	$C_{30}H_{22}$
MW	382.5
space gp	$P2_1/c$
cell dimens:	
a/Å	7.736 (1)
b/Å	10.965 (2)
c/Å	23.242 (3)
β/deg	93.96 (2)
V/Å^3	1966.8 (6)
Z	4
ρ_{calc}/g cm^{-3}	1.29
μ(Mo Kα)/cm^{-1}	0.37
no. of unique reflcns	3501
no. of reflcns with $I \geq 2\sigma(I)$	2653
R	0.042
R_w	0.056
w^{-1}	$\sigma_F{}^2 + 0.000289F^2$

Oxidation of **7** with selenium dioxide[9] in xylene gave a low yield of **2** and mostly **5**. Likewise, an analogous oxidation of **9** gave a low yield of *anti*-**3** and mostly **4**.

In conclusion, the titanium-induced reductive coupling of **5** to give **6** represents a novel application of the reaction in the series of overcrowded, strained PAH's.[24]

Stereochemistry of 6. The X-ray crystal structure analysis of **6** showed the crystal to belong to the space group $P2_1/c$. The refinement was carried out to $R = 0.042$ and $R_w = 0.056$ (Experimental Part and Table I). The structure of **6** (Tables I and II; Figure 1a) is that of a 9,10-diphenylanthracene with ethano bridges from the 1- and 5-positions of the anthracene ring to the nearest ortho positions of the substituent phenyl groups. The ethano bridges are on the same side of the anthracene ring; i.e., the compound has the chiral syn conformation with approximate C_2 symmetry (Figure 1b). Bridges on opposite sides of the anthracene ring would give the centrosymmetric anti form (Figure 1b). The strain in the syn form leads to some notable distortions. The anthracene moiety adopts bowl shape with angles of 9.2, 12.5, and 21.6° between rings A and B, A and C, and B and C, respectively

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Table II. Positional Parameters for Non-Hydrogen Atoms in 6 (Estimated Standard Deviations in the Least Significant Digits Shown in Parentheses)

atom	x	y	z
C1	0.2177 (3)	–0.0438 (2)	0.4562 (1)
C2	0.1955 (3)	–0.1095 (2)	0.4058 (1)
C3	0.2515 (3)	–0.0619 (2)	0.3551 (1)
C4	0.3333 (2)	0.0510 (2)	0.35579 (9)
C4a	0.3598 (2)	0.1175 (2)	0.40694 (8)
C4b	0.4558 (2)	0.2368 (2)	0.40482 (7)
C4c	0.6162 (2)	0.2359 (2)	0.37849 (8)
C5	0.7037 (3)	0.1227 (2)	0.37123 (9)
C6	0.8604 (3)	0.1186 (2)	0.3484 (1)
C7	0.9391 (3)	0.2263 (2)	0.3315 (1)
C7a	0.8638 (2)	0.3383 (2)	0.33571 (8)
C7b	0.6955 (2)	0.3467 (2)	0.35948 (7)
C8	0.9711 (2)	0.4458 (2)	0.31862 (9)
C9	0.9484 (2)	0.5646 (2)	0.35140 (9)
C9a	0.7877 (2)	0.6277 (2)	0.32813 (8)
C10	0.7951 (3)	0.7390 (2)	0.2995 (1)
C11	0.6489 (3)	0.7905 (2)	0.2718 (1)
C12	0.4931 (3)	0.7297 (2)	0.27102 (8)
C13	0.4820 (3)	0.6206 (2)	0.30040 (8)
C13a	0.6276 (2)	0.5688 (2)	0.33056 (7)
C13b	0.6016 (2)	0.4562 (2)	0.36484 (7)
C13c	0.4658 (2)	0.4595 (2)	0.40295 (7)
C14	0.4090 (2)	0.5750 (2)	0.42302 (7)
C15	0.2929 (2)	0.5827 (2)	0.46375 (8)
C16	0.2220 (2)	0.4756 (2)	0.48549 (8)
C16a	0.2640 (2)	0.3619 (2)	0.46735 (8)
C16b	0.3932 (2)	0.3489 (2)	0.42515 (7)
C17	0.1831 (3)	0.2570 (2)	0.4973 (1)
C18	0.3010 (3)	0.1470 (2)	0.51047 (9)
C18a	0.2986 (2)	0.0698 (2)	0.45753 (9)

(Figure 2). Rings A and D and A and E form angles of 53.0 and 53.1°, respectively.

Molecular mechanics calculations starting with the crystal structure lead to an energy-minimized structure with a calculated strain energy of 8.00 kcal/mol, rather similar to the crystal structure. The best fit of the carbon atoms in the two structures was obtained with a root-mean-square difference of 0.14 Å, the deviations being due to a somewhat more shallow bowl shape of the anthracene ring in the calculated structure. The Ar–C–C–Ar dihedral angles in the ethano bridges are 79.5 and 83.2° in the crystal structure and 77.9 and 78.9° in the calculated structure.

Similar calculations with a starting geometry obtained by reflecting the coordinates of one phenyl ring and of the adjacent ethano bridge in the plane of the central ring of the anthracene moiety lead to an energy-minimized structure with an approximate center of symmetry and with the ethano bridges in an anti arrangement, 1.39 kcal/mol higher in energy than the syn minimum. Since the syn form of 6 is chiral, its entropy is R ln 2 higher than that of the anti form (other things being equal), which contributes 0.41 kcal/mol to the free energy difference at 298 K. The total difference (1.8 kcal/mol) corresponds to 4.5% of the anti form at ambient temperature. The energy difference is underestimated, since no resonances of an anti form can be seen in the ^{1}H NMR spectrum of 6 (vide infra). However, it is likely that the anti form is a high-energy intermediate on the pathway for racemization of the syn form. Both the syn and the anti forms contain two stereogenic units[25] of biaryl type. In the syn form, they are *R*,*R* or *S*,*S*, and in the anti, *R*,*S* (meso).

The 300-MHz ^{1}H NMR spectrum of 6 in $CDCl_3$ consists of a complex set of resonances for the aromatic protons (see the Experimental Part), and of two multiplets in the intensity ratio 1:3 for the bridge protons, but no signals ascribable to a second conformer are detectable. In order to determine the barrier to ring inversion, the ^{1}H NMR spectrum was also recorded at elevated temperatures in benzophenone solution. At 120 °C, when no exchange effects could be discerned, the bridge proton resonances were quite similar to those in $CDCl_3$ solution, and they were iteratively analyzed as an ABCD system, giving the parameters found in Table III. The ^3J values for the bridge protons were calculated by the equation derived by Haasnoot et al.[26] (Table III), by using the dihedral angles shown in Figure 2. This leads to the assignment of the bridge protons given in Table III. The order of the geminal coupling constants, $|J_{AB}| < |J_{CD}|$, is in agreement with this assignment, when the orientation of the respective CH_2 groups with respect to the neighboring aromatic rings is considered (Figures 6 and 7, supplementary material).[27] The high-field position of the H81 resonance is due to screening by the nearby phenyl ring D.

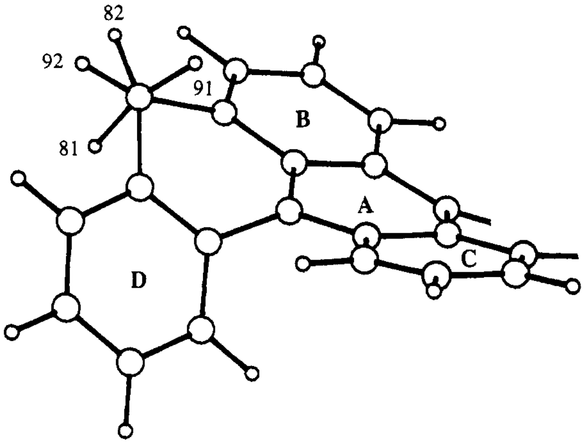

Figure 2. Projection along the C9–C8 bond in (*R*,*R*)-6. Ring E and the adjoining bridge have been removed for the sake of clarity.

With increasing temperature, the bridge proton resonances broaden but at 169 °C the spectrum is still far from coalescence. Simulation of the exchange-broadened spectra, assuming ABCD $\rightleftharpoons$ BADC exchange, gives the free energy barrier as 22.9 ± 0.1 kcal/mol. The rate constants are found in Table V (supplementary material).

A likely mechanism for the observed exchange process could involve the centrosymmetric anti form as a high-energy intermediate. In a critical step, one of the ethano bridges passes through an eclipsed arrangement, whereafter the attached phenyl ring D in a more or less coupled movement goes through the plane of the anthracene ring C, leading to the anti form of 6. In a second step the same process is performed by the other ethano bridge and phenyl ring E, leading to the enantiomer of the original syn form of 6. On the basis of this assumed mechanism, the free activation energies given in Table III refer to the *syn*-(+)–*syn*-(–) exchange (transmission coefficient 0.5).

The barrier to *syn*-(+)–*syn*-(–) exchange for 6 obtained in the NMR experiment indicates that the compound should be resolvable into enantiomers. A chromatographic experiment with a column packed with swollen, microcrystalline triacetylcellulose (TAC; see the Experimental Part) gave a chromatogram with well-separated peaks both in the UV and in the polarimeter trace, but the UV trace did not revert to the base line between the peaks. This is indicative of a complete enantiomer separation accom-

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Table III. Experimental Chemical Shifts, Experimental and Calculated Coupling Constants, and Assignment of Protons in the Ethano Bridges of 6 (Solvent Benzophenone)[a]

chem shift/Hz (300 MHz)		coupling const/Hz						
		exptl				calcd[b]		
			B	C	D		H-91	H-92
ν_A	886	A	∓12.0	±0.5	±5.0	H-81	0.82	6.89
ν_B	1060	B		±12.0	±0.7	H-82	12.25	0.97
ν_C	1060	C			∓14.0			
ν_D	1052							

assignment: A = H-81, B = H-82, C = H-91, D = H-92

[a] For numbering, see Figure 2. [b] With Θ(81,91) = 163.0°, Θ(81,92) = −78.4°, Θ(82,91) = −80.5°, and Θ(82,92) = 38.1°, from the X-ray structure.

Table IV. UV and CD Spectral Data of 6 and UV Spectral Data of 15 (9,10-Diphenylanthracene[29]) (Solvent Ethanol)

compound	λ_{max}/nm (ϵ, $\Delta\epsilon$)
6 (UV)	439.5 (9900), 416.5 (9750), 391 s[a] (5800), 275 (67 300), 195 (142 000)
15 (UV)[b]	392 (10 700), 372 (11 000), 354 (7100), 337 (3300), 322 s (1300), 259 (105 000), 226 (20 500)
(−)-**6** (CD)	437 (−6.2), 414.5 (−6.2), 396 s (−3.5), 380 s (−1.24), 305 (+4.22), 259.5 (−37.6), 222 (−55.5)

[a] Shoulder. [b] From ref 28.

panied by partial racemization on the column. When the experiment was repeated with the column cooled to 5 °C, complete base-line separation was observed and practically pure enantiomers could be collected in a cooled receiver.

The thermal racemization of the first eluted enantiomer, (−)-**6**, was followed by monitoring the intensity of the strong CD band at 222 nm in an ethanol solution from the TAC column in a thermostated cell. The free energy barrier to (−)-**6** → (+)-**6** exchange was found to be 22.6 ± 0.05 kcal/mol. The rate constants are found in Table V (supplementary material). The agreement with the NMR results is quite satisfactory, considering the different solvents. Assuming no solvent effect, an activation entropy of ca. −2.6 eu is calculated, which if anything is probably too positive for the assumed mechanism.

The ultraviolet spectrum of **6** (Figure 3; Table IV) shows a striking similarity to that of 9,10-diphenylanthracene (**15**; Table IV),[28] although the transitions in **6** appear at lower energies. This difference may be due to smaller angles between the phenyl and anthracene rings in **6** (53.1°) than in **15** (67°),[29] but substituent effects of the ethano bridges in positions 1 and 5 of the anthracene moiety of **6** may also contribute, as may the nonplanarity of the anthracene moiety in **6**. Still, it should be possible to interpret the UV and CD spectra of **6** with reference to the transitions in anthracene and in **15**. The band system in the range 390–440 nm is ascribed to the ^1L_a transition, polarized along the short axis of anthracene.[30,31] The long-axis-polarized ^1L_b transition is probably weak and overlapped by the ^1L_a band. A band near 360 nm in the MCD spectrum of anthracene has been assigned to the ^1L_b transition.[32] The strong band observed at 253 nm in the UV spectrum of anthracene has been assigned to the long-axis-polarized ^1B_b transition.[30] The strong bands at 275 and 259 nm in the UV spectra of **6** and **15**, respectively, most likely have the same origin. A much weaker band at 221 nm in the spectrum of anthracene has been assigned to the short-axis-polarized ^1B_a transition.[30] This probably corresponds to the band at 226 nm in the spectrum of **15**, and possibly to a shoulder in the same region in the spectrum of **6**.

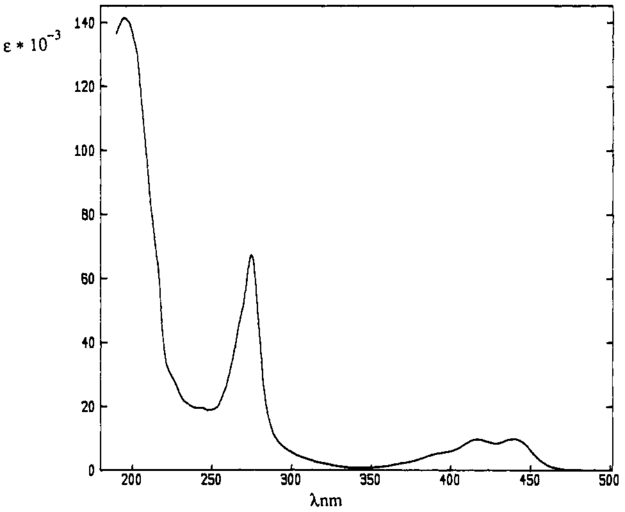

Figure 3. UV spectrum of **6** in ethanol.

The spectra of **6** and **15** and in particular the CD spectrum of **6** may be discussed in terms of interactions between the transitions in the benzene and anthracene chromophores in the "composite molecule" model.[33] In this, the important interactions are of two kinds.

One is between collinear or nearly collinear transitions, like the ^1L_a transitions in the benzene and anthracene chromophores. In **6**, these are not exactly aligned with the chromophore axes because of the effects of the ethano bridges, but this effect may be neglected in the first approximation. Interaction between, e.g., the ^1L_a transitions in the three chromophores gives rise to three new combinations, among which the one with all component moments in the same direction will have the lowest energy and highest intensity. These transitions are inherently chiral in **6**, and for symmetry reasons the low-energy, in-phase combination should follow the rule established by Mislow et al.[34] for the corresponding transition in bridged biphenyls, with a positive Cotton effect for the *R* configuration.

The second type of interaction is between transitions polarized along the long axis in anthracene and perpendicular to the pivot bond in the benzene chromophore. The directions of these transitions will also be influenced by the substituents in **6**, but as before we neglect this effect. This type of interaction can be treated with the coupled-oscillator technique.[35] Both types of interactions

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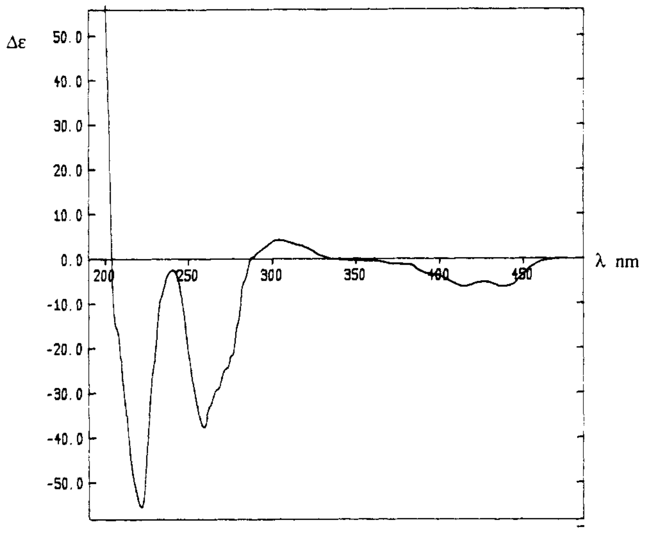

Figure 4. CD spectrum of (−)-**6** in ethanol.

increase in strength when the energies of the transitions involved become more equal. Interactions between nearly perpendicularly polarized transitions (^1L_b and ^1L_a) may be neglected.

In the following, the CD bands of (−)-**6** (Figure 4) will be analyzed in terms of the interactions discussed above. The low-energy ^1L_a combination will have mainly anthracene transition character, and the negative sign of the 380–440-nm band system indicates that (−)-**6** has the *S,S* configuration. The corresponding combination of benzene ^1L_a and anthracene ^1B_a transitions could be responsible for the strong negative CD band at 220 nm and confirms the configuration proposed above. The treatment of the ^1L_b and ^1B_b transitions in the coupled-oscillator model was performed with the matrix technique derived by Schellman and co-workers.[36] This technique requires as input in the present case transition energies, strengths and directions of electric transition moments, and transition charge densities (Table VI, supplementary material), and the derivation was performed as previously described.[37] The calculations were performed on a 9,10-diphenylanthracene with +53° dihedral angles between phenyl and anthracene rings (*S,S*), and the transition moments were localized in the centra of the rings. The calculations predict a medium–strong positive band at the long-wavelength side of the benzene ^1L_b transition and a similar negative band on the short-wavelength side of the anthracene ^1B_b transition. A very weak positive band is predicted for the anthracene ^1L_b transition. The stronger bands may be identified with CD bands at 305 and 270 nm, respectively. The latter appears as a shoulder on the side of the strong band at 259.5 nm, the remainder of which may have a contribution from a higher energy ^1L_a combination.

Evidently, the agreement reached in the discussion of all transitions in the near-UV region gives some credence to the assignment of (−)-**6** to the *S,S* configuration.

Experimental Part

Reductive Coupling of 5. (a) $TiCl_4$/Zn/Pyridine. This reaction, like those under b and c, was carried out under an argon atmosphere in a 500-mL three-necked round-bottomed flask equipped with a reflux condenser (protected from moisture), a dropping funnel, and a magnetic stirrer. Freshly distilled dry THF (distilled over sodium diphenyl ketyl, 220 mL) was added to the flask and the resultant mixture cooled to −5 °C. Dropwise slow injection of $TiCl_4$ (8.2 mL, 74.6 mmol) using a plastic syringe with continuous stirring gave a yellow complex, which was treated with Zn dust (10.0 g, 153 mmol). The temperature was gradually raised to room temperature and kept for another 1 h to give a greenish suspension. The mixture was refluxed for 5 h to complete the reduction, giving a green–black suspension. After being cooled to 0 °C, the mixture was treated with pyridine (5 mL), followed by dropwise addition over 4 h of a solution of ketone **5** (14.56 g, 70 mmol) in dry THF (60 mL). The resulting mixture was refluxed for 36 h. The disappearance of the starting material was monitored by TLC. After being cooled to room temperature, the mixture was added to dichloromethane (300 mL), stirred for 20 min, and treated with aqueous HCl (0.1 N) to give two layers. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. After the organic layers were dried ($MgSO_4$), the solvents were removed in vacuo. The crude products were dissolved in dichloromethane (yellow-green fluorescence) and chromatographed on a silica column, using a heptane–dichloromethane gradient (up to 30% dichloromethane) as eluent. The following successive fractions were eluted.

(1) Compound **6**: 3.5 g, 26% yield; yellow crystals; purification by sublimation at 50–180 °C (0.1 mm) afforded red crystals (yellow powder); mp 253 °C; R_f (silica, C_5H_{12}–CH_2Cl_2 (4:1)) 0.79; ^1H NMR (300 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.8, 0.9 Hz, 2 H), 7.35 (m, 4 H), 7.23 (m, 4 H), 7.12 (dd, *J* = 8.8, 5.3 Hz, 2 H), 7.08 (d, br, *J* = 7.1 Hz, 2 H), 3.51 (m, 6 H), 2.97 (m, 2 H); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 143.04 (s), 139.60 (s), 137.00 (s), 135.38 (s), 135.07 (d, *J* = 162 Hz), 133.12 (s), 129.01 (s), 127.81 (d, *J* = 162 Hz), 127.44 (d, *J* = 157 Hz), 126.49 (d, *J* = 158 Hz), 126.34 (d, *J* = 164 Hz), 125.19 (d, *J* = 164 Hz), 123.23 (d, *J* = 164 Hz), 40.72 (t, *J* = 128.7 Hz), and 33.06 (t, *J* = 129.4 Hz); fluorescence (EtOH) (λ_{ex} 416 nm) λ_{max} 480 nm; MS (153 °C, % P) *m/e* 383 (32), 382 (100), 191 (13). Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.07; H, 6.06.

(2) Compound **7**: 4.5 g, 33% yield; recrystallization from toluene gave colorless crystals; mp 271–272 °C (lit. mp 271.5–272.5 °C,[17] 275–276 °C[18]); R_f (silica, C_5H_{12}–CH_2Cl_2 (4:1)) 0.60; ^1H NMR (200 MHz, $CDCl_3$) δ 7.066 ($H_4H_{4'}H_5H_{5'}$, dd, *J* = 7.5, 1.4 Hz), 6.961 ($H_3H_{3'}H_6H_{6'}$, dt, *J* = 7.3, 1.3 Hz), 6.777 ($H_2H_{2'}H_7H_{7'}$, dt, *J* = 7.4, 1.4 Hz), 6.527 ($H_1H_{1'}H_8H_{8'}$, dd, *J* = 7.6, 1.0 Hz), 4.772 ($H_9H_{9'}$, s), [3.750 ($4H_{CH_2}$, s), 3.037 ($4H_{CH_2}$, s), ($2H_{10}2H_{11}$, $2H_{10'}2H_{11'}$)]; ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 139.39, 139.30, 131.91, 130.08, 126.37, 125.15, 60.81 (C_9), 33.98 ($C_{10}C_{11}$); MS (190 °C, % P) *m/e* 386 ($C_{30}H_{26}^+$, 1), 194 (62), 193 (100), 191 (53), 178 (89), 165 (31), 115 (74).

(3) Yellowish powder: fluorescent; unidentified; R_f (silica, C_5H_{12}–CH_2Cl_2 (4:1)) 0.33.

(4) $(Pyridine)_2ZnCl_2$ (eluted from the column by methanol): 3.0 g; mp 201 °C (from $CHCl_3$) (lit.[22] mp 205.8–206 °C).

(b) $TiCl_4$/$LiAlH_4$. Freshly distilled dry THF (120 mL) was cooled to 0 °C in the reaction flask. After injection of $TiCl_4$ (2.1 mL, 19 mmol), $LiAlH_4$ (1.14 g, 30 mmol) was added in portions and the mixture was gradually heated to room temperature and stirred for 30 min. The resulting suspension was treated by a dropwise addition of a solution of **5** (3.12 g, 15 mmol) in dry THF (100 mL) with stirring, and the mixture stirred for 6 h at room temperature and refluxed for 24 h. The mixture was cooled to 5 °C and treated with aqueous HCl (2 N, 60 mL). The crude product was filtered off and triturated successively with heptane and diethyl ether (to remove the starting ketone). The resulting white greenish crude product was recrystallized from toluene to give **7**: 2.0 g, 69%; colorless crystals; mp 274 °C, identical with **7** obtained in the previous reaction. No traces of **2** and **6** were present in the crude product.

(c) $TiCl_3$/$LiAlH_4$. $TiCl_3$ (3.12 g, 20 mmol) was added to the flask and the mixture treated dropwise with dry THF (100 mL). After the contents were cooled to −5 to 0 °C, $LiAlH_4$ (0.38 g, 10 mmol) was added in small portions and the mixture was refluxed with stirring for 15 min to give a black suspension. A solution of **5** (4.16 g, 20 mmol) in dry THF (110 mL) was then added dropwise with stirring to the cooled (0 °C) suspension. The resulting mixture was gradually heated to room temperature and

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refluxed for 10 h. After being cooled to room temperature, it was poured into water (300 mL) and treated with aqueous HCl (2 N, 50 mL) with stirring. The mixture was extracted with CH_2Cl_2, the organic layer was dried ($MgSO_4$), and the solvents were removed in vacuo. The remaining crude product was triturated with diethyl ether. Recrystallization from toluene afforded **7** as colorless crystals: mp 274 °C; 2.4 g, 63% yield. No traces of **2** and **6** were present in the crude product.

***anti*-10,10′,11,11′-Tetrahydro-5,5′-bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylidene) (2).** A mixture of **7** (0.200 g, 0.52 mmol) in dry xylene (20 mL) was treated with selenium dioxide (0.200 g, 1.82 mmol) and refluxed with magnetic stirring for 24 h. A red suspension was formed. After cooling, CH_2Cl_2 (50 mL) was added and the mixture was filtered through a cellulose layer, with use of a sintered glass filter. The solvents were evaporated in vacuo, and the crude product was chromatographed on a silica column, with hexane–diethyl ether (95:5) as eluent. The first fraction gave **2**: 0.055 g, 28% yield; colorless crystals; mp 310 °C. Recrystallization from $CHCl_3$ gave large, colorless crystals: mp 315 °C[13] (lit.[9b] mp 307 °C); ^1H NMR (200 MHz, $CDCl_3$) δ 7.118 (4 H, d, $J = 7.5$ Hz), 7.002 (4 H, m), 6.793 (8 H, m), 3.725 ($4H_{CH_2}$, m), 3.036 ($4H_{CH_2}$, m), ($2H_{10}2H_{11}2H_{10'}2H_{11'}$); ^{13}C NMR (50.29 MHz, $CDCl_3$) δ 140.84, 139.98, 138.35 ($C_{4a}C_{8a}C_9C_{9a}C_{10a}C_{4a'}C_{8a'}C_{9'}C_{10a'}$), 129.10, 128.80, 126.71, 125.41 ($C_1C_2C_3C_4C_5C_6C_7C_8C_{1'}C_{2'}C_{3'}C_{4'}C_{5'}C_{6'}C_{7'}C_{8'}$), 32.84 ($C_{10}C_{11}C_{10'}C_{11'}$); *MS* (170 °C, % P) *m*/*e* 385 (18), 384 (54), 193 (22), 192 (41), 116 (100). Anal. Calcd for $C_{30}H_{24}$: C, 93.75; H, 6.25. Found: C, 93.45; H, 6.55.

The second fraction gave ketone **5**, 0.100 g, 46% yield. The NMR spectrum of the crude product indicated that none of the syn isomers were formed.

Reductive Coupling of 4. (a) $TiCl_4$/Zn/Pyridine. The reaction was carried out analogously to the reductive coupling of **5**, starting with **4** (7.2 g, 34.9 mmol), $TiCl_4$ (4.1 mL, 37.3 mmol), Zn dust (5.0 g, 76.5 mmol), pyridine (5.0 mL), and THF (350 mL). The crude mixture of products was chromatographed on a series of silica columns with C_6H_6–CH_2Cl_2 gradient (up to 20% CH_2Cl_2) to give the following products.

(1) Compound **9**: 3.0 g, 45% yield; mp 325 °C from $CHCl_3$ (lit.[9b] mp 327 °C, 315–316 °C,[23a] 334 °C[23b]). ^1H NMR (200 MHz, $CDCl_3$) δ 7.234 ($H_4H_5H_{4'}H_{5'}$, dd, $J = 7.6, 1.6$ Hz), 7.063 ($H_{10}H_{11}H_{10'}H_{11'}$, s), 7.017 ($H_3H_6H_{3'}H_{6'}$, dt, $J = 7.4, 1.5$ Hz), 6.889 ($H_2H_7H_{2'}H_{7'}$, dt, $J = 7.4, 1.5$ Hz), 6.621 ($H_1H_8H_{1'}H_{8'}$, dd, $J = 7.2, 1.4$ Hz), 4.730 ($H_9H_{9'}$, s); ^{13}C NMR (75.44 MHz, $CDCl_3$) δ 139.44, 134.18, 131.12, 130.23, 129.40, 127.96, 125.94, 51.70; MS (190 °C, % P) *m*/*e* 382 (2), 193 (21), 192 (56), 191 (100), 190 (45), 189 (52), 165 (50), 164 (11), 163 (16). Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 93.77; H, 5.61.

(2) *syn*-**3**: 0.7 g, 11% yield; mp 254 °C (from C_6H_6) (lit.[9] mp 255 °C), identical with an authentic sample prepared according to the literature procedure. MS (150 °C, % P) *m*/*e* 380 (100), 363 (9), 303 (6), 302 (7), 202 (30), 191 (32), 190 (45), 189 (26). Anal. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 94.49; H, 5.08.

(3) An unidentified product: 0.35 g, mp 247 °C; contains C_{45} (mass spectrum).

(4) An unidentified product: 0.1 g.

No traces of *anti*-**3** and **10** were present in the crude mixtures of products.

(b) $TiCl_3$/$LiAlH_4$. The reaction was carried out analogously to the reductive coupling of **5**, starting with **4** (4.12 g, 20 mmol), $TiCl_3$ (3.12 g, 20.2 mmol), $LiAlH_4$ (0.38 g, 10 mmol), and THF (220 mL). The crude product was triturated with diethyl ether and recrystallized from benzene to give **8**: 2.2 g, 58% yield; mp 327 °C (lit.[9b] mp 327 °C). No traces of *syn*-**3** or *anti*-**3** were present in the crude product.

***anti*-5,5′-Bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylidene) (3).** *anti*-**3** was prepared analogously to *anti*-**2** by oxidation of **7** with selenium dioxide in xylene and was obtained as colorless crystals: mp 330 °C (lit. mp 332 °C,[9] 324 °C[8]); 13% yield; MS (190 °C, % P) *m*/*e* 380 (100), 379 (69), 378 (49), 377 (66), 364 (36), 363 (64), 350 (34), 190 (69). Anal. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 94.43; H, 5.13. The major product of the reaction was ketone **4**, 57% yield.

X-ray Crystal Structure Analysis of Compound 6. Data were measured on an Enraf-Nonius CAD-4 automatic diffractometer. Mo K_α ($\lambda = 0.71669$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The standard CAD-4 centering, indexing, and data collection programs were used. The unit cell dimensions were obtained by a least-squares fit of 22 centered reflections in the range of $10 \geq \theta \geq 14°$.

Intensity data were collected by the ω–2θ technique to a maximum 2θ of 52°. The scan width, $\delta\omega$, for each reflection was $0.80 + 0.35 \tan\theta$. An aperture with a height of 4 mm and a variable width, calculated as $(2 + {}^1/_2 \tan\theta)$ mm, was located 173 mm from the crystal. Reflections were first measured with a scan of 4.12°/min. The rate of the final scan was calculated from the preliminary scan results so that the ratio $I/\sigma(I)$ would be at least 40 and the maximum scan time would not exceed 60 s. If in a preliminary scan $I/\sigma(I) > 2$, this measurement was used as the datum. Scan rates varied from 127 to 4.12°/min. Of the 96 steps in the scan, the first and the last 16 steps were considered to be background. During data collection the intensities of three standard reflections were monitored after every 1 h of X-ray exposure; 8% decay was observed. In addition, three orientation standards were checked after 100 reflections to check the effects of crystal movement. If the standard deviation of the *hkl* values of any orientation reflection exceeded 0.007, a new orientation matrix was calculated on the basis of the recentering of the 22 reference reflections.

Intensities were corrected for decay, Lorentz, and polarization effects. All non-hydrogen atoms were found by using the results of the MULTAN-78 direct-method analysis.[38] After several cycles of refinements the positions of the hydrogen atoms were found and added with a constant isotropic temperature factor of 0.05 Å to the refinement process. Refinement proceeded to convergence by minimizing the function $\sum w(|F_o| - |F_c|)^2$. A final difference Fourier synthesis map showed several peaks less than 0.2 e·Å^{-3} scattered about the unit cell without a significant feature.

The discrepancy indices, $R = \sum(|F_o| - |F_c|)/\sum F_o$ and $R_w = [\sum w(|F_o| - F_c|)^2/\sum w|F_o|^2]^{1/2}$ are presented with other pertinent crystallographic data in Table I. The fractional positional parameters are found in Table II, and important bond lengths and bond angles are given as supplementary material.

Molecular mechanics calculations were performed with the Allinger MM2 85 force field.[39,40] The input structures were generated with the interactive computer graphics program MOLBUILD.[40,41]

^1H and ^{13}C NMR spectra were recorded with Varian Model XL-300 and VXR-300 NMR spectrometers and a Bruker Model WP-Sy 200-MHz NMR spectrometer. The simulation of the exchange-broadened ^1H NMR spectra of **6** in benzophenone solution to obtain the rate constants k_{inv} (Table V, supplementary material) was performed by the DNMR-5 program.[42] The temperature scale of the instrument was calibrated by measuring the shift difference between the OH and CH_2 resonances of ethylene glycol.[43] The transverse relaxation time T_2 was assumed to be the same for all ethano protons and was evaluated with aid of a sharp signal in the solvent spectrum[44] and the free activation energies ΔG^* were calculated by the Eyring equation.[45]

The chromatographic resolution of 6 on TAC[46] was performed with the equipment described by Isaksson and Roschester.[47] The column was enclosed in a glass mantle, through which cooled ethanol (5 °C) was circulated. With ethanol–water

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(96:4, v/v) as the mobile phase, the chromatographic indices were as follows: $k'_{(-)}$, 2.39; $k'_{(+)}$ 7.26; α, 3.04.

The UV spectrum of 6 was recorded with a Cary Model 2290 spectrophotometer. **The CD spectrum** was recorded directly on the pure fractions from the TAC column, by a Jasco Model J-500 A spectropolarimeter. The recording of the spectrum (at 5 °C) and the racemization experiments were performed in a 0.1-cm water-jacketed cell attached to a circulation thermostat. The concentrations of the solutions were estimated from their UV spectra.

Racemization Experiments. The first-order rate constants (k_{rac}) for racemization of 6 were obtained by monitoring the intensity of the strong CD band at 222 nm as a function of time at 19.3, 34.5, and 50.0 °C. The free activation energies for ring inversion were calculated by the Eyring equation[45] with $k_{inv} = 0.5k_{rac}$.

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Supplementary Material Available: Figures showing the stereoscopic view of the syn form of 6 from MM2 calculations (Figure 5), projection along the C9–C9a bond in (*R*,*R*)-6 (Figure 6), and projection along the C8–C7a bond in (*R*,*R*)-6 (Figure 7), with ring E and the adjoining bridge removed for clarity, and tables of rate constants and free energy barriers for the (−)-6→(+)-6 exchange (Table V), input data for the calculation of CD spectra (Table VI), hydrogen atom positional parameters (Table VII), thermal parameters and estimated standard deviations (Table VIII), and important bond lengths and bond angles (Table IX) (9 pages). Ordering information is given on any current masthead page.

Notes

Synthesis of Polyisocyanide Compounds via α-Metalation Reactions

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Introduction

α-Metalated isocyanides were first prepared over 20 years ago[1] and have since become useful reagents in organic synthesis.[2a–c] Because the isocyanide group is readily hydrolyzed to the corresponding amine, metalated isocyanides provide a convenient means of nucleophilic introduction of α-aminoalkyl groups into organic molecules. For example, the reaction of metalated 2-isocyanopropionic ester with benzylbromide provides, following acid hydrolysis, α-methylphenylalanine.[3] Alternatively, reactions of α-metalated isocyanides with various electrophilic reagents such as ketones, thioketones, Schiff bases, etc., permit an efficient route to the resulting heterocycles (oxazolines, thiazolines, imidazolines, etc.).

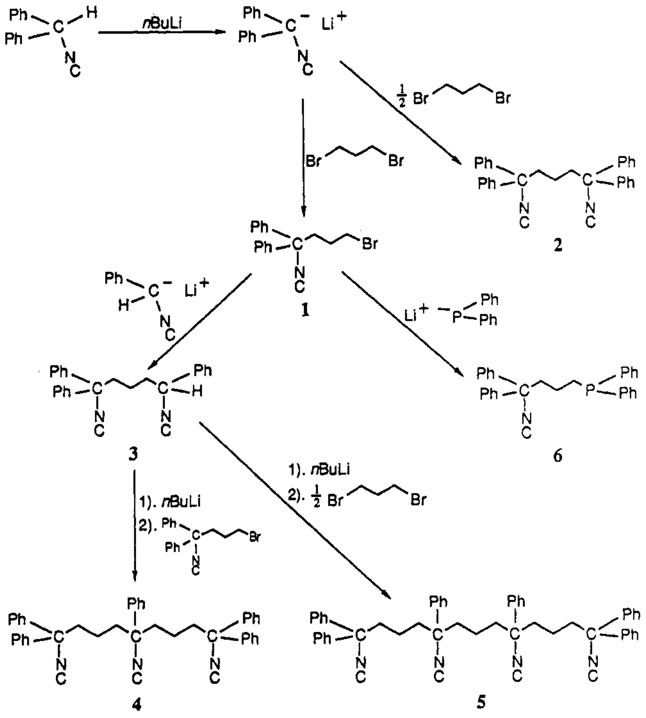

Figure 1. Synthetic reaction scheme for the preparation of compounds 1–6.

Our interest in isocyanides lies in the ability of the isocyanide group to form complexes with transition metals. In large part because of their ability to stabilize metal complexes in a variety of oxidation states, the organometallic chemistry of isocyanide ligands is extensive and well documented.[4a–c] Of particular interest are binuclear complexes of rhodium and iridium in which the square planar metals are held in close proximity by bridging isocyanide groups. Since the first report of $Rh_2(bridge)_4(BF_4)_2$ in 1977 (bridge = 1,3-diisocyanopropane) as a potential solar energy storage device,[5] the electrochemical and photophysical properties of several d^8–d^8 isocyanide-bridged, binuclear complexes have been studied.[6] In an attempt to extend this chemistry to longer

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