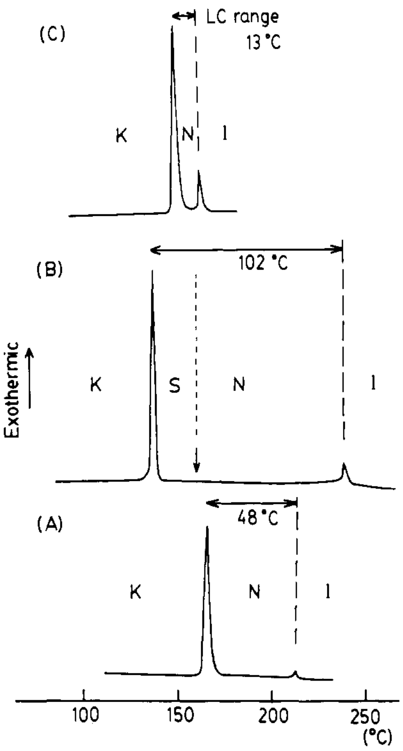

Figure 1. DSC thermograms of (A) **2Sz**; (B) the 1:1 complex of **2Sz** and **4BA** (an arrow indicates the nematic to smectic transition); and (C) **4BA** on heating.

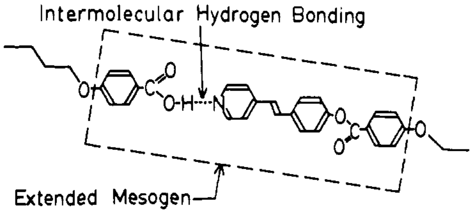

Figure 2. The proposed structure of the new mesogen formed by intermolecular H bonding between **4BA** and **2Sz**.

ring. The sharp melting transition peak of DSC also suggests the existence of a 1:1 complex between **4BA** and **2Sz**.[8]

Coleman et al.[9] have reported that hydrogen bonding between the pyridine rings and carboxylic moieties was preferred over that between two carboxylic acid units in blends of poly(ethylene-*co*-methacrylic acid) and poly(2-vinylpyridine). We have also observed a similar behavior in blends of poly(4-vinylbenzoic acid) and poly(4-vinylpyridine); our observation[10] that a 1:1 blend of these two polymers has a glass transition temperature T_g = 233 °C, which is 30 °C higher than the calculated weight average T_g, also supports the existence of a strong hydrogen bond between pyridine and carboxylic acid moieties. Further support for the preferred formation of N···HO hydrogen bonds between carboxylic acids and amines can be found in X-ray studies of compounds such as nicotinic acid.[11]

It is worthwhile noting that, in our system, a single H bond is sufficient to preserve the linearity of the new extended mesogen, in contrast to the two H bonds that were required in the case of the dimeric monosaccharides[2,3] and aromatic acid[4] dimers.

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(8) A referee has kindly pointed out that the H bonding of the system may be dynamic. At the present time, our data does not allow us to either endorse or reject this suggestion; X-ray experiments in progress only show that the 1:1 complex is favored in the crystalline state.

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The Stereochemistry of the 1,4-Addition of Dibromocarbene to 1,2-Dimethylenecycloheptane

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The 1,4-addition of carbenes to 1,3-dienes has a long and controversial history.[1] Only in recent years, and in rather specific constellations, a number of apparently genuine examples of this reaction have been reported.[2] In these cases, arguments for a concerted pathway have been presented but alternative, stepwise sequences cannot yet be excluded with the desired degree of certainty. We now wish to report stereochemical evidence supporting a concerted, one-step course of the reaction.

Theory predicts that if this reaction is concerted and controlled by orbital symmetry, it must occur in a disrotatory fashion if it is a linear process and conrotatory for a nonlinear process.[3] A suitable 1,3-diene for the investigation of this aspect is (Z,Z)-[1′,2′-D_2]-1,2-dimethylenecycloheptane (**2**) which we have synthesized from the zirconacycle **1**[4] by stereospecific cleavage of the zirconium–carbon bonds with deuterosulfuric acid (17 equiv, room temperature, immediate workup), followed by stereospecific removal of the trimethylsilyl groups by treatment with trifluoroacetic acid (2 equiv) in methylene chloride for 10 min (Scheme I). The isotopic and configurational integrity of **2** was proven by ^{1}H NMR and mass spectroscopy.[5]

The reaction of **2** with dibromocarbene (from bromoform and potassium *tert*-butoxide in pentane at room temperature) yielded the expected[2e] 9:1 mixture of the 1,2-adduct **3** and the 1,4-adduct **4** in 80% total yield; note that it has previously been shown that there is no secondary rearrangement of **3** to **4**.[2e] ^{1}H NMR spectroscopy of **4** does not allow a distinction between the two stereoisomers **4a** and **4b** as both have only one kind of the allylic protons H(8,10); they appear as a broad singlet at δ = 3.50 ppm. Therefore, the mixture of **3** and **4** was reduced with 1 equiv of triphenyltin hydride to give a mixture of stereoisomers of **5** and **6** (Scheme I) which was separated by preparative gas chromatography and investigated by 400 MHz ^{1}H NMR spectroscopy; the region of the diagnostic bishomoallylic proton H(9) of **6** is presented in Figure 1a. In principle, **6** might consist of three stereoisomers: **6a** (derived from the conrotatory adduct **4a**) and

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(5) **2**: ^{1}H NMR (90 MHz, CDCl$_3$) δ = 4.74 (br s, 2 H), 2.35 (m, 4 H), 1.60 (m, 6 H); MS m/z (rel intensity) 124 (43), $M^{\bullet+}$. Both spectra indicated a D_2-incorporation of approximately 95%. 1,2-Dimethylenecycloheptane:[6] ^{1}H NMR (90 MHz, CDCl$_3$) δ = 5.14 (m, 2 H), 4.73 (m, 2 H), 2.33 (m, 4 H), 1.60 (m, 6 H). **6b** + **6c** (1:1): ^{1}H NMR (400.1 MHz, CDCl$_3$, 296 K) **6b** δ = 4.47 (t of quintet, $^3J_{HH}$ = 4.0 Hz, $^3J_{HD}$ = 1.0 Hz, 2 H, H(9)), 2.75 (m, 2 H, H(8)/H(10)), 2.08 (m, 4 H), 1.62 (m, 6 H); **6c** δ = 4.48 (br t, $^3J_{HH}$ = 7.2 Hz, 2 H, H(9)), 2.97 (m, 2 H, H(8)/H10)), 2.08 (m, 4 H), 1.62 (m, 6 H). MS m/z (rel intensity) 216 (6, with isotope pattern), $M^{\bullet+}$. D-incorporation (estimated by comparison of the HRMS spectrum of **6b**/**6c** with that of the unlabeled parent **6H**) 90.6% D_2, 5.9% HD, 3.5% H_2. 9-Bromobicyclo[5.3.0]dec-1(7)-ene (**6H**): ^{1}H NMR (250.1 MHz, CDCl$_3$) δ = 3.69 (A_2B_2X system, δ_A = 2.77, δ_B = 3.00, δ_X = 4.49, J(AB) = 15.0 Hz, J(AX) = 4.0 Hz, J(BX) = 7.0 Hz, 5 H), 2.11 (m, 4 H), 1.60 (m, 6 H); MS m/z (rel intensity) 214 (9, with isotope pattern), $M^{\bullet+}$, 135 (58), 107 (37), 91 (100); HRMS calcd for $C_{10}H_{15}{}^{79}Br$ 214.0310, found 214.0357.

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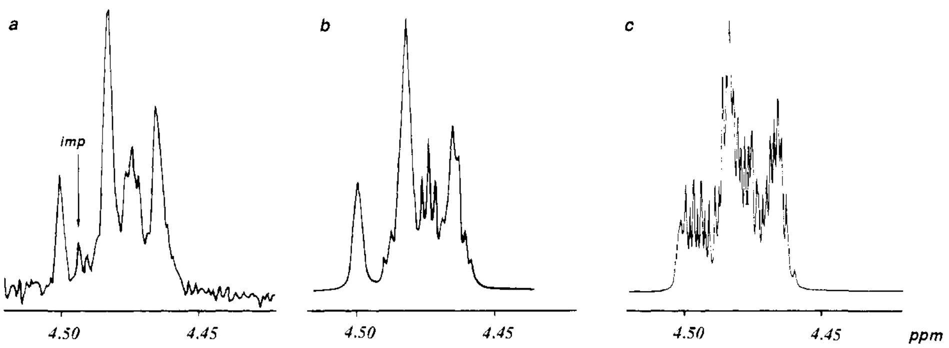
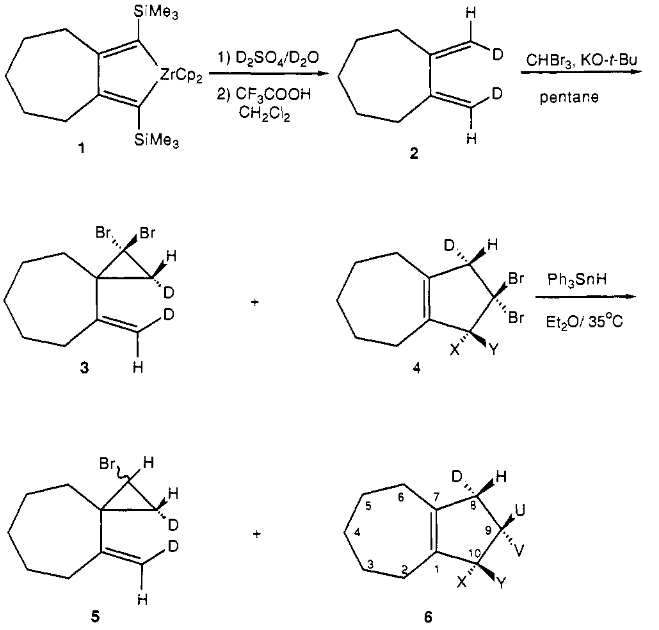


Figure 1. 400 MHz ^{1}H NMR spectrum of **6** in the region of H(9): (a) experimental spectrum, (b) simulated spectrum of a 1:1 mixture of **6b,c**, (c) simulated spectrum of a statistical (2:1:1) mixture of **6a,b,c**.

Scheme I[a]



[a] **a**: X = H, Y = D, U = H, V = Br; **b**: X = D, Y = H, U = Br, V = H; **c**: X = D, Y = H, U = H, V = Br.

a 1:1 mixture of **6b**[5] and **6c** (derived from the disrotatory adduct **4b**); the respective signals of H(9) were simulated with the PANIC program[7] with ^2J(H,H) = 15.0 Hz, Z ^3J(H,H) = 7.0 Hz, and E ^3J(H,H) = 4.0 Hz (taken from the spectrum of the unlabeled **6H**[5]) and the relation J(H,H) ≈ 6.51 J(H,D).[8] As shown in Figure 1b, the simulated spectrum of a 1:1 mixture of **6b** and **6c** reproduces the experimental one[9] quite well; for comparison, the calculated spectrum of a random, statistical mixture (**6a**:**6b**:**6c** = 2:1:1) is presented in Figure 1c. Because of the relatively low D_2-incorporation (90.6%), the difference spectrum from Figure 1 (parts b and a) was irregular and did not permit a conclusion on the possible presence of minor quantities of **6a**. However, the addition of increasing percentages of the simulated spectrum of **6a** to that in Figure 1b showed that approximately 15% **6a** would have been detectable. This implies a disrotatory stereospecificity of the 1,4-addition for 70% or more. Thus, a necessary requirement for concertedness of the 1,4-addition of a carbene has been established. At the same time, we have shown that the process, if concerted, is (predominantly) of the linear type.[3]

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Registry No. 1, 122924-25-8; **2**, 122901-97-7; **3**, 122901-98-8; **4a**, 122901-99-9; **4b**, 122902-00-5; **5**, 122902-01-6; **6a**, 122902-02-7; **6b**, 122902-03-8; **6c**, 122902-04-9; **6H**, 122902-05-0; dibromocarbene, 4371-77-1; 1,2-dimethylenecycloheptane, 58738-52-6.

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Diastereoselective Nucleophilic Addition to Coordinated Cyclohexadienyl Rings in Chiral Manganese Complexes

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The transition-metal-mediated synthesis of difunctionalized cyclohexadienes by nucleophilic addition to coordinated arenes has been investigated with a number of systems:[1-4] $(\text{arene})_2\text{Fe}^{2+}$, CpCo(arene)^{2+}, and $(\text{arene})\text{Mn(CO)}_2\text{L}^+$ (L = CO, PR_3). The manganese reactions generally involve single nucleophilic addition to give $(\text{cyclohexadienyl})\text{Mn(CO)}_2\text{L}$ complexes which are reactivated toward a second nucleophilic attack by conversion to $(\text{cyclohexadienyl})\text{Mn(CO)(NO)L}^+$ cations.[4] It has been shown[5]

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