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DIASTEREOSELECTIVE FORMATION OF CHIRAL 2,2'-SPIROBIBENZ[d]CHROMENE DERIVATIVES. EVIDENCE FROM CIRCULAR DICHROISM AND CRYSTALLOGRAPHIC DATA

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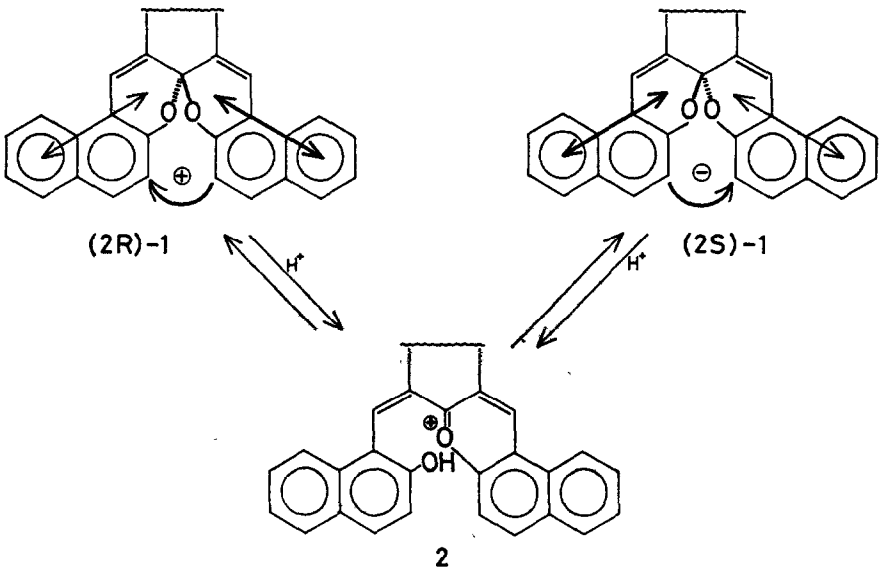
Abstract: Condensation of optically active ketones, (3R)-methylcyclohexanone and 5α-cholestan-3-one, with 2-hydroxy-1-naphthaldehyde brings about formation of chiral 2,2'-spirobibenz[d]chromene derivatives with diastereoselectivity 75% and 100%, respectively. Absolute configuration of the newly formed chiral center was determined through the application of the exciton chirality method and for the 2,2'-spirobibenz[d]chromene derivative of (3R)-3-methylcyclohexanone confirmed by the X-ray crystallographic study.

Introduction

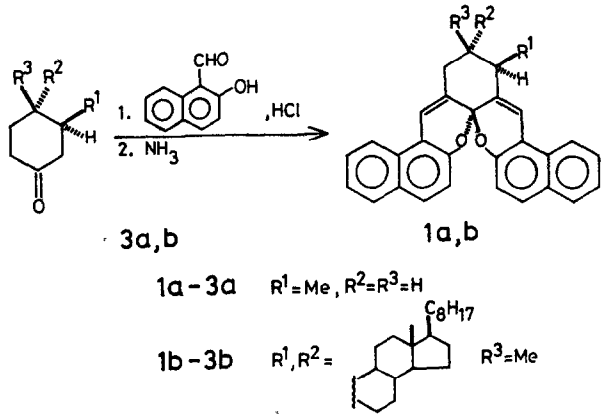
Condensation of 2-hydroxy-1-naphtaldehyde with α,α'-unsubstituted ketones in the acid solution, followed by treatment with the base, brings about formation of 2,2'-spirobibenz[d]chromene derivatives 1 which have C_2-symmetry and are axially chiral. A number of racemic derivatives 1 have been prepared from achiral ketones[1-6] and their properties examined. It was found that certain spiropyran derivatives related to 1 show remarkable property of thermochromism developing an intense violet color on heating in polar solvents and reverting to colorless at room temperature. Similar effect was observed on irradiation of 1 with ultraviolet light at -100°C[7]. Furthermore, 2,2'-spirobibenz[d]chromene derivatives 1 on treatment with strong acids form readily red-violet colored benz[d]chromenium salts 2, which can be converted to 1 on neutralization with a base. These observations permit the assumption that in 2,2'-spirobibenz[d]chromenes 1 both enantiomers i.e. (2R) and (2S) are in equilibrium, through the intermediacy of the polar form 2 (Scheme 1). This form (2 or mesomeric forms) can be generated through the action of heat or ultraviolet light in the presence of proton donors or by the action of acidic centers. When the parent ketone 3 used for preparation of 1 is chiral, the configuration of the new chiral center generated in 1 at C(2) should be controlled by the chiral center present in 1. The effect of asymmetric induction in the above reaction is the subject of this report.



Scheme 1

Results and Discussion

Two chiral, non-racemic ketones, (3R)-3-methyl-cyclohexanone (**3a**) and 5α-cholestan-3-one (**3b**), were condensed with 2-hydroxy-1-naphthaldehyde in the presence of hydrochloric acid, according to the general procedure[1-6]. The intermediate salts **2** were treated with ammonia to give, after purification by silicagel chromatography, crystalline products **1a** and **1b**[8](Scheme 2).



Scheme 2

Circular dichroism examination of the spiropyrans 1a and 1b reveals a series of weaker Cotton effects in the range 350–280 nm and strong Cotton effects, typical for chiral intramolecular exciton interaction of aromatic chromophores, at shorter wavelengths[9,10] (Table 1).

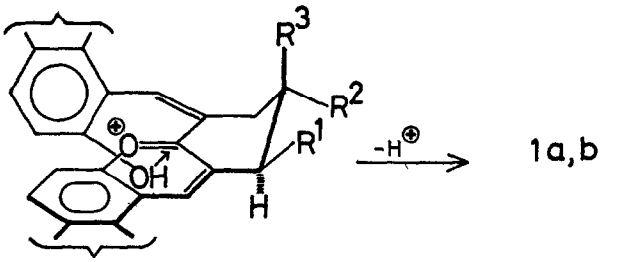
Table 1. CD and UV data for 1a and 1b (in dioxane) and for 1b in dioxane acidified with hydrochloric acid

	CD, Δε (nm)	UV, ε (nm)
1a	−18.6 (346)	14,600 (344)
	−7.3 (332)	12,500 (330)
	−9.7 (312)	24,000 (310)
	+5.5 (302)	22,800 (297)
	+12.6 (290)	
	+14.2 (281)	17,300 (283)
	+280 (246)	165,300 (246)
	A = +470	
	−190 (230)	106,000sh (239)
1b	−15.6 (348)	14,400 (345)
	−3.9 (334)	12,500 (331)
	−4.1 (314)	22,200 (311)
	+13.4 (304)	20,700 (298)
	+20.8 (294)	
	+19.8 (285)	14,500 (286)
	+326 (247)	135,700 (246)
	A = +568	
	−242 (231)	96,000sh (240)
1b × HCl	−2.6 (556)	21,700 (556)
	+2.2 (412)	9,000 (436)
	−1.6 (345)	9,700 (332)
	−3.0 (314)	12,300 (301)
	+3.6 (286)	12,200 (290)
	+11.6 (230)	70,000 (231)

These bisignate Cotton effects, located at 246–247 nm and 230–231 nm, belong to the allowed, long axis polarized, ^1B_b transition in the benz[d]chromene chromophore. The corresponding UV maximum for this transition is located at 246 nm, with the shoulder at 239–240 nm. The splitting of the UV band at 246 nm due to exciton interaction of the two benz[d]chromene chromophores with the lower energy band having higher intensity indicates that the electric transition moments of the two chromophores form obtuse angle[11].

From the sign of the exciton Cotton effect of 1a and 1b it is possible to determine the absolute configuration of the newly formed chiral center at C(2). Positive lower energy and negative higher energy CD bands require positive torsional angle between the two transition moments, as defined in

Scheme 1, according to the principles of the exciton chirality method[12]. This requirement is met for the (2R) absolute configuration of the new chiral center in 1a and 1b. Large amplitudes of the exciton Cotton effects of 1a (A = +470) and (A = +568) suggest high diastereoselectivity in the formation of the 2,2'-spirobibenz[d]chromene system from 3a and 3b. Examination of the proton NMR spectra of 1a and 1b allows to determine diastereomeric excess of these products. While 1b shows only signals of the protons due to one diastereoisomer, 1a displays signals of the protons due to the major diastereoisomer (2R) and minor diastereoisomer (2S). The occurence of the minor diasteroisomer (2S) is most straightforwardly determined from the presence of the two doublets of the methyl group in the ^{1}H NMR spectra of 1a. The higher intensity, lower field signal at δ 1.44 belongs to the (2R)-diastereoisomer in which the methyl group occupies pseudoequatorial position, while the lower intensity, higher field signal at δ 1.24 is due to the (2S)-diasteroisomer, having pseudoaxial methyl group. From the integration of these signals a ratio 7:1 of the (2R) to (2S) diastereoisomers of 1a can be determined (d.e. 75%). The ratio of the two diastereoisomers of 1a remains unchanged in solution after recrystallization, heating to the melting point or formation of the salt 2a with hydrochloric acid and its decomposition with ammonia. Furthermore, chromatography of 1a and 1b on silicagel brings about formation of slight pink coloration of the adsorbed compound, characteristic of the ionic form 2. These facts suggest that 2,2'-spirobibenz[d]chromenes 1a and 1b in solution can be epimerized readily at C(2) through the intermediacy of the ionic form 2, formation of which can presumably be catalyzed by acidic centers present in the medium. However, in the equilibrium products 1a and 1b with (2R)-configuration are strongly favoured over those with (2S)-configuration. In fact, 1b exists as a sole diastereoisomer (2R) and for 1a a diastereomeric excess 75% has been determined. The effect of asymmetric induction in the formation of 1a and 1b from 2 is visualized in Scheme 3.



Scheme 3

In the envelope conformation of the central ring in **2** the tendency for *re*-face attack of the phenolic hydroxy group on the sp^2-hybridized C(2) atom apparently results from the preference for the formation of the C-O bond from the less hindered α-side of the molecule.

In order to confirm the assignment of absolute configuration and to obtain details of the structure of 2,2'-spirobibenz[d]chromenes, X-ray crystallographic analysis of (2R)-**1a** has been performed.

Crystal structure of 1a

The final atomic parameters of non-hydrogen atoms are listed in Table 2.

Table 2. Fractional atomic coordinates and anisotropic temperature factors (Å^2). The y-coordinate of C(2) was fixing the origin and was not refined

atom	x/a	y/b	z/c	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
O(1)	-0.1065(4)	0.0432(3)	0.8715(3)	0.080(2)	0.075(2)	0.077(2)	0.001(2)	0.022(2)	0 004(2)
C(2)	0.0522(6)	0.0057	0.8670(5)	0.076(3)	0.070(3)	0.064(3)	0.001(2)	0.011(2)	-0.003(2)
C(3)	0.0606(6)	-0.1063(4)	0 8747(5)	0.079(4)	0.069(3)	0.071(3)	-0.001(2)	0.013(3)	0.001(3)
C(4)	-0.0730(6)	-0.1586(4)	0.8224(5)	0.090(4)	0.075(3)	0.070(3)	0.005(3)	0.024(3)	0.005(3)
C(5)	-0.2283(6)	-0.1089(5)	0.7643(5)	0.063(3)	0.089(4)	0.067(3)	-0.000(3)	0.016(3)	-0.006(3)
C(6)	-0.3700(7)	-0.1588(5)	0.6855(6)	0.086(4)	0.105(5)	0.073(3)	0.007(3)	0.024(3)	-0.011(4)
C(7)	-0.3693(8)	-0.2619(5)	0.6497(6)	0.109(5)	0 097(5)	0.096(4)	-0.008(4)	0.027(4)	-0.022(4)
C(8)	-0.5090(9)	-0.3062(6)	0.5723(7)	0.098(5)	0.148(6)	0.111(5)	-0.015(5)	0.027(4)	-0.042(5)
C(9)	-0.6471(11)	-0.2542(8)	0.5240(8)	0.120(7)	0 162(8)	0.119(6)	-0.027(6)	0.016(5)	-0 046(6)
C(10)	-0 6554(8)	-0.1559(8)	0.5601(8)	0.077(4)	0.180(8)	0.115(5)	0.019(6)	0.013(5)	-0.008(5)
C(11)	-0.5177(8)	-0.1038(7)	0.6431(6)	0.069(4)	0.148(6)	0.088(4)	0.005(4)	0.019(3)	-0.005(4)
C(12)	-0.5202(7)	-0.0009(6)	0.6810(7)	0.072(4)	0.135(6)	0.110(5)	0 022(4)	0.021(3)	0.015(4)
C(13)	-0.3817(7)	0.0466(5)	0 7544(6)	0 085(4)	0 105(4)	0.095(4)	0.005(3)	0.030(3)	0.014(4)
C(14)	-0.2393(6)	-0.0081(5)	0.7925(5)	0.068(3)	0.086(4)	0.073(3)	0.005(3)	0.012(3)	0 002(3)
C(17)	0.2244(6)	-0.1446(4)	0.9523(6)	0.079(4)	0.073(3)	0.098(4)	0.015(3)	0.020(3)	0.012(3)
C(18)	0.2472(8)	-0.2579(4)	0.9390(7)	0.111(5)	0.079(4)	0.135(5)	0.010(4)	0.019(4)	0.014(4)
C(16)	0.2529(7)	-0.1113(4)	1.1059(5)	0.108(4)	0.087(4)	0.084(4)	0.016(3)	0.003(3)	0.001(3)
C(15)	0.2103(8)	-0.0014(4)	1.1231(5)	0.134(5)	0.090(4)	0.071(3)	0 010(3)	0.007(3)	0.001(4)
C(14')	0.1107(5)	0.1317(4)	0.7118(5)	0.067(3)	0 072(3)	0.067(3)	0.003(3)	0.016(2)	0.003(3)
C(13')	0.0685(6)	0.1667(4)	0.5721(5)	0.087(4)	0.084(4)	0.062(3)	0 008(3)	0.013(2)	0.008(3)
C(12')	0.0981(6)	0.2641(4)	0.5441(5)	0.098(4)	0.085(4)	0.065(3)	0.013(3)	0.019(3)	0 012(3)
C(11')	0.1715(7)	0.3302(4)	0.6522(5)	0.095(4)	0.073(4)	0.075(3)	0.012(3)	0 026(3)	0.014(3)
C(10')	0.2011(8)	0.4310(5)	0.6253(6)	0 136(5)	0.076(4)	0.091(4)	0.013(3)	0.046(4)	0.009(4)
C(9')	0.2743(9)	0.4959(5)	0.7311(7)	0 177(7)	0.073(4)	0.111(4)	0.002(3)	0.077(5)	0 005(4)
C(8')	0.3199(8)	0.4607(5)	0 8676(7)	0.138(5)	0.080(4)	0.104(4)	-0 020(3)	0.046(4)	-0.027(4)
C(7')	0 2949(7)	0.3629(4)	0 9018(5)	0 113(4)	0 075(4)	0.080(3)	-0 007(3)	0 027(3)	-0 009(3)
C(6')	0.2192(6)	0.2939(4)	0 7944(5)	0 088(4)	0 065(3)	0.076(3)	0 000(3)	0.026(3)	-0 004(3)
C(5')	0 1864(6)	0.1920(4)	0 8221(5)	0 079(3)	0.064(3)	0.069(3)	0 006(2)	0.019(3)	0.006(3)
C(4')	0 2329(6)	0.1442(4)	0.9620(5)	0 083(3)	0.075(3)	0 066(3)	0.001(2)	0.012(2)	-0.002(3)
C(3')	0.1742(6)	0 0567(4)	0 9838(4)	0 087(3)	0 073(3)	0.062(3)	0 001(2)	0 013(2)	0 000(3)
O(1')	0 0797(3)	0.0319(3)	0 7316(3)	0.078(2)	0 073(2)	0.061(2)	0.003(2)	0 016(1)	0.001(2)

A perspective view of molecule **1a** and the labeling of its atoms is presented in Fig.1. The terminal atoms of the molecule have considerably larger thermal-vibrational parameters than the atoms in its centre. This can be caused by large lattice-mode vibrations of the molecules - due to weak van der Waals cohesion forces in this crystal - and can be a reason of relatively high estimated standard deviations of the atomic coordinates and some increase in the R-values.

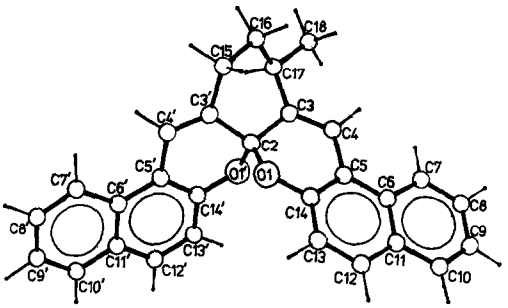


Figure 1. A perspective view[13] of molecule 1a as present in crystalline state.

Table 3. Bond lengths (Å) and valency angles (°)

O(1)	-C(2)	1.441(6)		C(4)	-C(3)	-C(17)	128 2(5)
O(1)	-C(14)	1 385(6)		C(3)	-C(4)	-C(5)	121 3(5)
C(2)	-C(3)	1 495(5)		C(4)	-C(5)	-C(14)	117.4(5)
C(2)	-C(3')	1.509(6)		C(4)	-C(5)	-C(6)	124 3(5)
C(2)	-O(1')	1 437(6)		C(6)	-C(5)	-C(14)	118 3(5)
C(3)	-C(4)	1 324(7)		C(5)	-C(6)	-C(11)	119 1(6)
C(3)	-C(17)	1 505(7)		C(5)	-C(6)	-C(7)	122 2(5)
C(4)	-C(5)	1 462(7)		C(7)	-C(6)	-C(11)	118 7(6)
C(5)	-C(6)	1.428(7)		C(6)	-C(7)	-C(8)	119 9(6)
C(5)	-C(14)	1 379(8)		C(7)	-C(8)	-C(9)	122 4(8)
C(6)	-C(7)	1.417(9)		C(8)	-C(9)	-C(10)	119 8(8)
C(6)	-C(11)	1.423(9)		C(9)	-C(10)	-C(11)	121 9(8)
C(7)	-C(8)	1 378(9)		C(6)	-C(11)	-C(10)	117 2(7)
C(8)	-C(9)	1 345(12)		C(10)	-C(11)	-C(12)	123 7(6)
C(9)	-C(10)	1.361(14)		C(6)	-C(11)	-C(12)	119.1(6)
C(10)	-C(11)	1 434(10)		C(11)	-C(12)	-C(13)	121.1(7)
C(11)	-C(12)	1.421(12)		C(12)	-C(13)	-C(14)	118.7(6)
C(12)	-C(13)	1 376(8)		C(5)	-C(14)	-C(13)	123.6(5)
C(13)	-C(14)	1.382(8)		O(1)	-C(14)	-C(13)	115.6(5)
C(17)	-C(18)	1 531(7)		O(1)	-C(14)	-C(5)	120.5(5)
C(17)	-C(16)	1.529(7)		C(3)	-C(17)	-C(16)	108 2(4)
C(16)	-C(15)	1 525(7)		C(3)	-C(17)	-C(18)	114 2(5)
C(15)	-C(3')	1 534(6)		C(18)	-C(17)	-C(16)	112 0(5)
C(14')-C(13')		1.406(6)		C(17)	-C(16)	-C(15)	113 5(4)
C(14')	-C(5')	1 376(6)		C(16)	-C(15)	-C(3')	113 0(4)
C(14')-O(1')		1 377(6)		C(5')	-C(14')-O(1')		121 5(4)
C(13')	-C(12')	1 361(8)		C(13')	-C(14')-O(1')		116 3(4)
C(12')-C(11')		1.404(7)		C(13')	-C(14')-C(5')		122 2(5)
C(11')-C(10')		1 403(8)		C(14')	-C(13')-C(12')		119 6(4)
C(11')	-C(6')	1 437(7)		C(13')	-C(12')-C(11')		121 1(5)
C(10')-C(9')		1 379(8)		C(12')	-C(11')-C(6')		119 5(5)
C(9')	-C(8')	1 381(9)		C(12')	-C(11')-C(10')		121 8(5)
C(8')	-C(7')	1 373(8)		C(10')	-C(11')-C(6')		118 8(5)
C(7')	-C(6')	1 429(7)		C(11')	-C(10')-C(9')		121 9(5)
C(6')	-C(5')	1 423(7)		C(10')	-C(9')	-C(8')	119 1(6)
C(5')	-C(4')	1 475(6)		C(9')	-C(8')	-C(7')	122.2(6)
C(4')	-C(3')	1 303(7)		C(8')	-C(7')	-C(6')	120 0(5)
				C(11')	-C(6')	-C(7')	118 0(5)
				C(7')	-C(6')	-C(5')	123.3(4)
C(2)	-O(1)	-C(14)	116 8(3)	C(11')	-C(6')	-C(5')	118 7(4)
O(1)	-C(2)	-O(1')	107 1(2)	C(14')	-C(5')	-C(6')	118 9(4)
O(1)	-C(2)	-C(3')	107 4(2)	C(6')	-C(5')	-C(4')	124 4(4)
O(1)	-C(2)	-C(3)	112 2(4)	C(14')	-C(5')	-C(4')	116 6(4)
C(3')	-C(2)	-O(1')	111 0(2)	C(5')	-C(4)	-C(3')	120 5(4)
C(3)	-C(2)	-O(1')	105 8(2)	C(15)	-C(3')	-C(4')	126 3(4)
C(3)	-C(2)	-C(3')	113 3(3)	C(2)	-C(3')	-C(4')	119 9(4)
C(2)	-C(3)	-C(17)	113 0(4)	C(2)	-C(3')	-C(15)	113 8(4)
C(2)	-C(3)	-C(4)	118 7(5)	C(2)	-O(1')	-C(14')	116 1(3)

Table 4. Selected torsion angles (

C2	-O1	-C14	-C5	27 8(7)
C2	-O1	-C14	-C13	-156 5(5)
C14	-O1	-C2	-O1'	73 5(5)
C14	-O1	-C2	-C3'	-167 3(4)
C14	-O1	-C2	-C3	-42.1(5)
O1	-C2	-O1'	-C14'	73 0(4)
O1	-C2	-C3'	-C15	91 5(4)
O1	-C2	-C3	-C4	30 0(6)
C3'	-C2	-O1'	-C14'	-43 9(5)
C3	-C2	-C3'	-C15	-33 0(5)
O1'	-C2	-C3'	-C4'	31 0(6)
C3'	-C2	-C3	-C17	-24 4(6)
C2	-C3	-C17	-C18	-169 4(4)
C2	-C3	-C17	-C16	65 1(5)
C2	-C3	-C4	-C5	-3.0(8)
C4	-C3	-C17	-C18	14 8(8)
C17	-C3	-C4	-C5	172 6(5)
C3	-C4	-C5	-C6	169 1(5)
C3	-C4	-C5	-C14	-13 5(8)
C4	-C5	-C14	-O1	0 8(8)
C4	-C5	-C6	-C7	-3.6(9)
C12	-C13	-C14	-C5	-1 7(9)
C3	-C17	-C16	-C15	-45 8(6)
C18	-C17	-C16	-C15	-172.6(5)
C17	-C16	-C15	-C3'	-9 2(6)
C16	-C15	-C3'	-C2	50 6(6)
C16	-C15	-C3'	-C4'	-132 4(6)
C5'	-C14'	-O1'	-C2	30 0(6)
C13'	-C14'	-O1'	-C2	-153 2(4)
C13'	-C14'	-C5'	-C6'	1 7(7)
O1'	-C14'	-C5'	-C4'	0 2(7)
C13'	-C12'	-C11'	-C6'	1 3(8)
C7'	-C6'	-C5'	-C4'	-3 0(8)
C6'	-C5'	-C4'	-C3'	167 8(5)
C14'	-C5'	-C4'	-C3'	-14 2(7)
C5'	-C4'	-C3'	-C15	-179 5(5)
C5'	-C4'	-C3'	-C2	-2 6(7)

The bond lengths and valency angles are listed in Table 3; they are in good agreement with the expected values. There are also no significant differences between the corresponding bond lengths and valency angles of the two moieties of this quasi-symmetrical molecule [with respect to the quasi-two-fold axis

passing through C(2)]. Selected torsion angles are listed in Table 4 - they indicate that there are no significant differences in conformation of the two moieties of the molecule, except for ring C(2)-C(3')-C(15)-C(16)-C(17)-C(3) and its adjacent bonds [compare torsion angle C(5)-C(4)-C-(3)-C(17) with its primed counterpart]. The conformation of this ring can be described as intermediate between boat and twist-boat - the asymmetry parameters[14] of these forms are: $\Delta C_s^{17,3'} = 17.5$, $\Delta C_s^{2,3} = 23.0$, $\Delta C_2^{3,17} = 22.6$ and $\Delta C_2^{2} = 23.6°$. The two pyran rings have nearly identical 1,3-diplanar conformation. The χ^2 values for the least-squares planes fitted to the atoms of the unprimed and primed naphtalene substituents are 21.1 and 5.9, respectively . The dihedral angle between these planes equals 60.0(1)°. A stereoscopic view of crystal structure structure 1a is presented in Fig. 2.

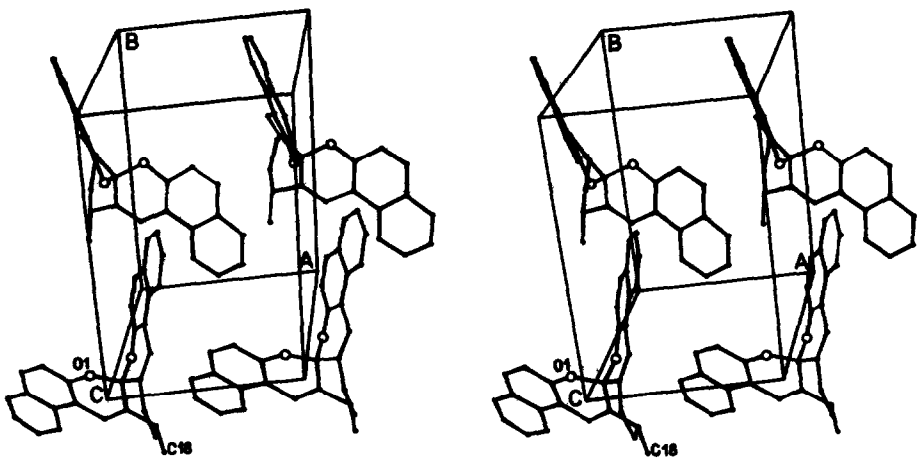


Figure 2. A stereoview[13] of the arrangement of molecules 1a in crystal.

In conclusion we have found that 2,2'-spirobibenz[d]chromene derivatives 1a and 1b are formed diastereoselectively from chiral ketones 3a and 3b, respectively. The asymmetric induction in the formation of the chiral spirocyclic center at C(2) apparently results from different thermodynamic stabilities of the two diastereoisomers, having (2R) and (2S) configuration. The equilibration of the two diastereoisomers occurs through the polar intermediate 2. Possible applications of the present results in designing new chiral molecules for asymmetric catalysis and chiral recognition phenomena are now under investigation.

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Experimental Section

General

Crystal Data for 1a at 292K: $C_{29}H_{22}O_2$, M_r=402.50, monoclinic $P2_1$, a=8.449(2), b=13.320(3), c=9.762(1) Å, β=103.41(1)°, V=1068,6(2) Å^3, Z=2, D_x=1.251 gcm^{-3}, F(000)=424e, $\lambda(CuK_\alpha)$=1.54178 Å, $\mu(CuK_\alpha)$=6.15 cm^{-1}. A colorless transparent cube, edge of 0.30 mm, a fragment cut off from a bigger crystal was used for data collection.

Data Collection and Reduction: a Syntex $P2_1$ diffractometer with graphite-monochromated CuK_α radiation, 2θ-θ scan ∓1° with a variable speed (2.0 - 29.3°min^{-1}), maximum 2θ=116°(h: -9/9, k: 0/14, l: 0/10). Two control reflections monitored every each 200 current measurements showed no systematic variation in their intensities throughout the data collection. Lp corrections only, $I \geq 1.96\sigma_I$ criterion for observed reflections.

Structure Solution and Refinement: direct methods[15], correct enantiomorph assigned according to the chemical information on the absolute configuration of carbon atom (R)-C(17), the positions of all hydrogen atoms were recalculated from the molecule geometry after each cycle of refinement, the H-atoms were assigned isotropic temperature factors and were not refined. Weighted ($w=\sigma_F^{-2}$) full-matrix least-squares refinement[16] of anisotropic model for non-hydrogen atoms [17]. The final R=0.054, wR=0.054, S=1.1, max. and min. ΔF: 0.12 and -0.15 e/A^3, max. shift/e.s.d.=0.1. Scattering factors incorporated in SHELX-76 were used, all the calculations were performed on an IBM-XT Turbo computer.

Spectral Data: NMR spectra were obtained with a Bruker 270 MHz spectrometer. Chemical shifts are reported as δ values relative to internal Me_4Si. IR spectra were recorded with a Perkin Elmer 180 instrument. CD and UV spectra were obtained with a Jobin-Yvon III dichrograph and a Cary 219 spectrometer, respectively.

Condensation of (R)-3-methylcyclohexanone (3) with 2-hydroxy-1-naphthaldehyde.

A solution of 0.62 ml (5 mmol) (R)-3-methylcyclohexanone (3a) and 1.72g (10 mmol) 2-hydroxy-1-naphthaldehyde in ethanol (10 ml) was saturated with gaseous hydrochloric acid and left standing overnight. The deeply colored crystals of the hydrochloride salt 2a were collected and washed with diethyl ether, yield 95% . A suspension of the salt in dichloromethane was treated with gaseous

ammonia and the discolored solution filtered through a pad of alumina. Removal of the solvents gave 1a as yellowish solid (yield was nearly quantitative). The 2,2'-spirobibenz[d]chromene derivative 1a was crystallized from ethyl acetate, m.p. 197-199°; $[\alpha]_D^{21}$ +117.0 (c=1,$CHCl_3$); ^1H NMR ($CDCl_3$):8.22 (d, 1H, J=7.5 Hz), 8.16 (d, 1H, J=7.5 Hz), 7.78 (d, 1H, J=7.5 Hz), 7.76 (d, 1H, J=7.5 Hz), 7.63 (t, 2H, J=9.0 Hz), 7.54 (t, 2H, J=7.5 Hz), 7.44 (s, 1H), 7.42 (m, 2H), 7.40 (s, 1H), 7.01 (d, 1H, J=9.0 Hz), 6.92 (d, 1H, J=9.0 Hz), 2.6-2.8 (m. 3H), 2.10 (dq, 1H, J=6.5 and 11.0 Hz), 1.50 (m, 1H), 1.24 and 1.42 (two d, 3H, J=6.5 Hz); IR (KBr): 3060, 1235, 935, 815 and 750 cm^{-1}.

Anal. Calcd. for $C_{29}H_{22}O_2$: C 86.54; H 5.51. Found: C 86.42; H 5.43.

Condensation of 5α-cholestan-3-one (3b) with 2-hydroxy-1-naphthaldehyde.

A solution of 387 mg (1 mmol) 5α-cholestan-3-one (3b) and 345 mg (2 mmol) 2-hydroxy-1-naphthaldehyde in ethanol (3 ml) was saturated with gaseous hydrochloric acid. After 24 hours the deeply colored solution was evaporated and the residue taken-up in dichloromethane. After treatment with gaseous ammonia the solution was filtered through a pad of alumina and the products separated by centrifugal chromatography on silicagel (solvent hexane - diethyl ether, 9:1). The 2,2'-spirobibenz[d]chromene derivative 1b was obtained as amorphous solid, m.p. 150-153°; $[\alpha]_D^{20}$ +245.0 (c=1, $CHCl_3$); ^1H NMR ($CDCl_3$): 8.23 (d, 1H, J=7.5 Hz), 8.14 (d, 1H, J=7.5 Hz), 7.80 (d, 1H, J=7.5 Hz), 7.76 (d, 1H, J=7.5 Hz), 7.62 (t, 2H, J=9.0 Hz), 7.54 (t, 2H, J=7.5 Hz), 7.41 (bs, 1H), 7.40 (t, 1H, J=7.5 Hz), 7.37 (t, 1H, J=7.5 Hz), 7.20 (bs, 1H), 6.98 (d, 1H, J=9.0 Hz), 6.90 (d, 1H, J=9.0 Hz), 2.89 (d, 1H, J=17 Hz), 2.59 (d, 1H, J=17 Hz), 2.50 (d, 1H, J=12 Hz), 1.0-2.1 (m, 24H), 0.95 (d, 3H, J=6.5 Hz), 0.87 (d, 6H, J=6.5 Hz), 0.85 (s, 3H) and 0.71 (s, 3H); IR (KBr): 3060, 1235, 945, 805 and 740 cm^{-1}.

Anal. Calcd. for $C_{49}H_{56}O_2$: C 86.93; H 8.34. Found: C 86.63; H 8.59.

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