Crystallographic Analysis of a Pair of Isolable Atropisomers of 2-Aryl Substituted Indoline Derivatives

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The crystal and molecular structures of isomeric compounds of 1-(4'-chlorobenzoyl)-2-(2''-hydroxynaphthyl)-3,3-Dimethylindoline have been determined by single crystal X-ray analyses as a pair of diastereomeric atropisomers due to restricted rotation about a Csp^3-Csp^2 bond.

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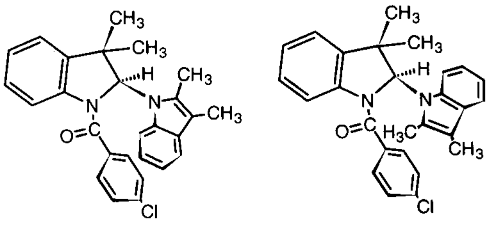
Isolation of atropisomers originated from restricted rotation about single bond has been an attractive subject to challenge for chemists. Many investigations have been performed to estimate the rotational barrier making use of dynamic nmr method. Oki and his associates carried out the systematic studies on triptycene and fluorene derivatives [1].

Recently, attention has been paid to the conformational isomers of some drugs from pharmacological view point [2]. Previously, we reported that pyrolysis of 1-(4'-chlorobenzoyl)-3,3-dimethylindolin-2-ylpyridinum chloride afforded two isomeric compounds **1a, 1b** of the same molecular formula $C_{27}H_{25}N_2OCl$ [3]. The spectral data [3,4] and X-ray diffraction analysis [5] indicated that **1a** and **1b** were the first example of diastereomeric atropisomers, which involved the restricted rotation about a Csp^3–Nsp^2 bond (Figure 1).



1a 1b

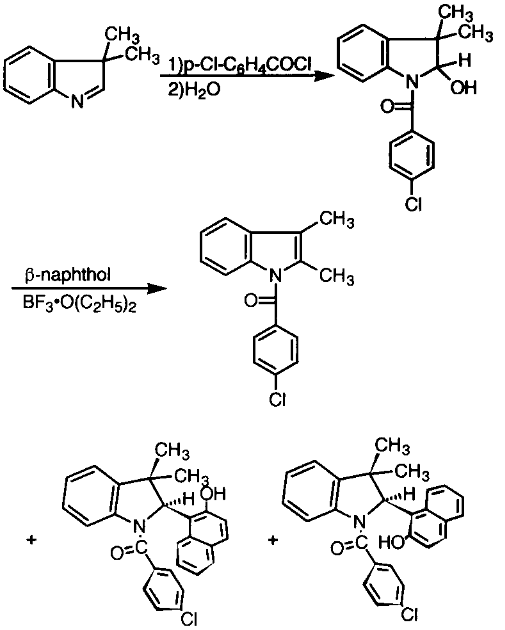
Figure 1

In the continuous studies, anologous isomerisms were observed in 2-aryl substituted indoline derivatives **2a, 2b** [6], in which the 2-substituent of **1** was replaced by 2-hydroxynaphth-1-yl group. These compounds were isolated as stable rotational isomers which might be due to restricted rotation about Csp^3-Csp^2 bond.

In this paper, we wish to present an unambiguous evidence for the molecular structures of **2a** and **2b** by X-ray crystallography.

Condensation of 1-(4'-chlorobenzoyl)-2-hydroxy-3,3-dimethylindoline with β-naphthol using $BF_3O(C_2H_5)_2$ as a catalyst in dioxane gave a mixture of two isomeric compounds, **2a** and **2b** (Scheme 1). The isomers were easily separated by chromatography on silica gel [7].

Scheme 1



2a 2b

Crystallization of **2a** and **2b** from ethanol-acetone by slow evaporation gave single crystals suitable for X-ray analysis. The structures were solved by direct method using the program MULTAN78 [8]. Block-diagonal Least-squares refinement gave a final R of 0.078 for **2a** and 0.062 for **2b**. Fractional atomic coordinates for **2a** and **2b** are given Table 1. The ORTEP [9] drawings and numbering system used in this paper are shown in Figure 2, and their bond lengths and angles are summarized in Tables 2 and 3 respectively.

Table 1

Fractional Atomic Coordinates [a] and Isotropic Temperature Factors (B) of **2a** and **2b** for Non-hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

2a

Atom	X/a	Y/b	Z/c	B [b]
Cl(1)	4356(3)	5951(2)	3090(2)	7.69(14)
C(2)	4130(7)	6508(7)	2121(6)	4.62(41)
C(3)	4617(7)	6392(8)	1686(6)	4.60(39)
C(4)	3489(7)	7015(8)	1825(7)	5.03(45)
C(5)	4458(6)	6829(7)	917(6)	3.69(35)
C(6)	3320(6)	7442(8)	1059(7)	4.08(38)
C(7)	3776(6)	7317(7)	581(6)	3.27(32)
C(8)	3589(6)	7796(7)	-234(6)	3.37(33)
O(9)	3458(4)	8607(4)	-283(4)	4.51(26)
N(10)	3568(4)	7317(5)	-925(5)	2.99(26)
C(11)	3521(6)	7676(7)	-1708(6)	3.13(32)
C(12)	3492(7)	8567(7)	-1965(6)	4.15(37)
C(13)	3470(7)	8718(8)	-2781(7)	4.62(39)
C(14)	3479(8)	8042(8)	-3331(7)	5.33(45)
C(15)	3476(7)	7159(9)	-3052(7)	5.44(46)
C(16)	3498(6)	6972(7)	-2257(6)	3.31(33)
C(17)	3544(7)	6073(7)	-1858(7)	4.14(40)
C(18)	2921(9)	5414(9)	-2363(8)	6.60(55)
C(19)	4332(9)	5670(8)	-1705(9)	6.64(59)
C(20)	3507(6)	6315(6)	-966(6)	3.11(33)
C(21)	2845(6)	5928(7)	-753(6)	3.03(31)
C(22)	2988(6)	5156(6)	-279(6)	3.16(32)
O(23)	3688(4)	4785(5)	-65(5)	4.35(26)
C(24)	2426(7)	4757(7)	-22(6)	3.93(39)
C(25)	1719(7)	5125(8)	-255(7)	4.28(41)
C(26)	1534(6)	5892(7)	-741(6)	3.35(33)
C(27)	798(6)	6264(8)	-977(7)	4.45(39)
C(28)	616(7)	7013(9)	-1435(7)	5.38(45)
C(29)	1165(7)	7455(8)	-1683(8)	5.73(44)
C(30)	1880(6)	7115(8)	-1491(6)	4.18(37)
C(31)	2106(6)	6319(7)	-999(5)	3.12(32)
Cl(1')	541(2)	5833(3)	-3384(2)	7.08(14)
C(2')	724(7)	6379(7)	-4205(7)	4.27(40)
C(3')	1342(7)	6945(9)	-4008(7)	5.67(46)
C(4')	264(7)	6216(7)	-5029(7)	4.35(40)
C(5')	1489(6)	7394(7)	-4648(6)	4.00(36)
C(6')	431(6)	6662(7)	-5657(6)	3.60(35)
C(7')	1041(6)	7252(6)	-5478(6)	3.39(34)
C(8')	1170(5)	7755(7)	-6177(6)	3.16(31)
O(9')	1186(5)	8573(5)	-6161(4)	4.81(28)
N(10')	1260(5)	7272(6)	-6814(5)	3.57(28)
C(11')	1276(5)	7655(7)	-7580(6)	3.15(31)
C(12')	1220(6)	8541(7)	-7840(7)	4.10(37)
C(13')	1274(7)	8722(8)	-8623(7)	5.05(42)
C(14')	1369(7)	8052(8)	-9120(7)	5.10(42)
C(15')	1430(7)	7159(7)	-8865(6)	4.32(38)
C(16')	1385(6)	6956(7)	-8078(6)	3.42(34)
C(17')	1395(6)	6048(7)	-7673(6)	3.58(34)
C(18')	2019(7)	5438(8)	-7721(7)	4.97(43)
C(19')	612(8)	5588(8)	-8118(8)	6.09(49)
C(20')	1459(6)	6296(6)	-6759(6)	3.20(35)
C(21')	2193(5)	6063(6)	-6047(5)	2.75(30)
C(22')	2161(6)	5280(7)	-5651(6)	3.71(36)
O(23')	1521(4)	4774(5)	-5919(5)	5.06(28)
C(24')	2789(7)	4968(7)	-4974(7)	4.27(40)
C(25')	3434(6)	5434(8)	-4717(6)	4.04(38)
C(26')	3491(6)	6253(7)	-5127(6)	3.74(35)
C(27')	4180(7)	6765(9)	-4836(7)	5.44(44)
C(28')	4249(7)	7561(10)	-5209(8)	5.67(47)
C(29')	3624(7)	7864(9)	-5883(8)	5.43(46)
C(30')	2559(6)	7398(7)	-6172(7)	3.90(37)
C(31')	2866(6)	6583(7)	-5796(6)	3.24(34)

Table 1 (continued)

2b

Atom	X/a	Y/b	Z/c	B [b]
Cl(1)	5639(1)	2731(3)	-76(1)	10.34(08)
C(2)	5524(3)	2491(7)	1201(4)	5.90(16)
C(3)	5457(3)	3755(6)	1626(4)	5.54(16)
C(4)	5489(3)	1279(6)	1746(5)	5.90(17)
C(5)	5342(3)	3835(5)	2625(4)	4.71(13)
C(6)	5364(3)	1370(5)	2738(4)	4.90(14)
C(7)	5280(2)	2634(4)	3182(3)	3.56(10)
C(8)	5141(2)	2686(4)	4250(3)	3.55(10)
O(9)	5631(2)	3100(4)	5007(3)	5.04(09)
N(10)	4472(2)	2184(3)	4368(3)	3.25(08)
C(11)	4235(2)	2059(4)	5316(3)	3.58(10)
C(12)	4631(3)	2401(5)	6329(4)	4.35(12)
C(13)	4256(3)	2216(6)	7124(4)	5.27(15)
C(14)	3531(3)	1685(6)	6926(4)	5.70(16)
C(15)	3151(3)	1346(6)	5920(4)	5.25(15)
C(16)	3506(2)	1548(4)	5113(4)	3.87(11)
C(17)	3198(3)	1244(5)	3957(4)	4.36(12)
C(18)	2391(3)	1840(7)	3537(5)	6.63(19)
C(19)	3191(4)	-317(6)	3767(5)	6.65(19)
C(20)	3805(2)	1931(4)	3450(3)	3.55(10)
C(21)	3580(2)	3238(4)	2809(3)	3.39(10)
C(22)	3542(2)	4495(4)	3288(3)	3.36(10)
O(23)	3627(2)	4548(3)	4346(2)	4.19(08)
C(24)	3410(2)	5752(5)	2708(4)	4.00(11)
C(25)	3309(3)	5720(5)	1650(4)	4.34(12)
C(26)	3318(2)	4462(5)	1110(3)	4.31(12)
C(27)	3209(3)	4442(7)	1(4)	5.72(16)
C(28)	3245(4)	3233(7)	-504(4)	6.53(19)
C(29)	3363(3)	1990(7)	44(4)	6.12(17)
C(30)	3458(3)	1969(5)	1116(4)	4.86(13)
C(31)	3447(2)	3202(5)	1693(3)	3.79(11)

[a] Positional parameters are multiplied by 10^4. [b] Thermal parameters are given the equivalent temperature factors (Å^2).

As can be seen in Figure 2, the conformations are nearly identical except for the disposition of the naphthyl group. This fact rules out a possibility that the atropisomerism is due to restricted rotation about the amide CO-N bond. The significant structural differences between the two isomeric compounds appear in the C(17)-C(20)-C(21)-C(22) dihedral angles, which were −97.2 and 76.1° for **2a** and **2b** respectively. The two compounds were determined as a Csp^3-Csp^2 type diastereomeric atropisomers caused by the barrier to rotation about C(20)-C(21).

As for the geometries except for the naphthyl groups, some common structural features were found. The C(17)-

Table 2

Bond Distances (Å) of **2a** and **2b** for Non-hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

		2a		**2b**
		Molecule 1	Molecule 2	
Cl(1)	-C(2)	1.755(11)	1.745(13)	1.741(06)
C(2)	-C(3)	1.371(20)	1.380(18)	1.363(09)
C(2)	-C(4)	1.362(17)	1.386(14)	1.382(09)
C(3)	-C(5)	1.394(15)	1.381(18)	1.378(08)
C(4)	-C(6)	1.380(16)	1.379(17)	1.378(09)
C(5)	-C(7)	1.412(14)	1.383(13)	1.392(07)
C(6)	-C(7)	1.380(18)	1.393(15)	1.379(07)
C(7)	-C(8)	1.486(14)	1.490(15)	1.484(07)
C(8)	-O(9)	1.228(12)	1.218(12)	1.227(05)
C(8)	-N(10)	1.361(13)	1.356(14)	1.348(06)
N(10)	-C(11)	1.406(13)	1.429(13)	1.415(06)
N(10)	-C(20)	1.495(12)	1.494(12)	1.503(05)
C(11)	-C(12)	1.390(15)	1.383(15)	1.388(06)
C(11)	-C(16)	1.392(14)	1.399(15)	1.374(06)
C(12)	-C(13)	1.388(17)	1.392(18)	1.387(08)
C(13)	-C(14)	1.376(17)	1.357(18)	1.374(09)
C(14)	-C(15)	1.398(18)	1.390(17)	1.371(08)
C(15)	-C(16)	1.362(17)	1.399(16)	1.379(08)
C(16)	-C(17)	1.489(15)	1.514(14)	1.511(06)
C(17)	-C(18)	1.541(17)	1.509(18)	1.542(07)
C(17)	-C(19)	1.535(20)	1.560(17)	1.531(08)
C(17)	-C(20)	1.579(16)	1.557(15)	1.565(07)
C(20)	-C(21)	1.523(17)	1.526(12)	1.518(06)
C(21)	-C(22)	1.375(13)	1.357(14)	1.379(06)
C(21)	-C(31)	1.430(14)	1.417(14)	1.426(06)
C(22)	-O(23)	1.356(13)	1.358(13)	1.360(05)
C(22)	-C(24)	1.406(18)	1.410(13)	1.424(06)
C(24)	-C(25)	1.365(17)	1.333(16)	1.356(07)
C(25)	-C(26)	1.380(15)	1.426(16)	1.411(07)
C(26)	-C(27)	1.414(15)	1.436(17)	1.420(07)
C(26)	-C(31)	1.440(16)	1.409(13)	1.429(07)
C(27)	-C(28)	1.333(17)	1.371(20)	1.353(09)
C(28)	-C(29)	1.406(20)	1.399(15)	1.391(09)
C(29)	-C(30)	1.367(17)	1.364(16)	1.376(08)
C(30)	-C(31)	1.427(14)	1.411(15)	1.415(07)

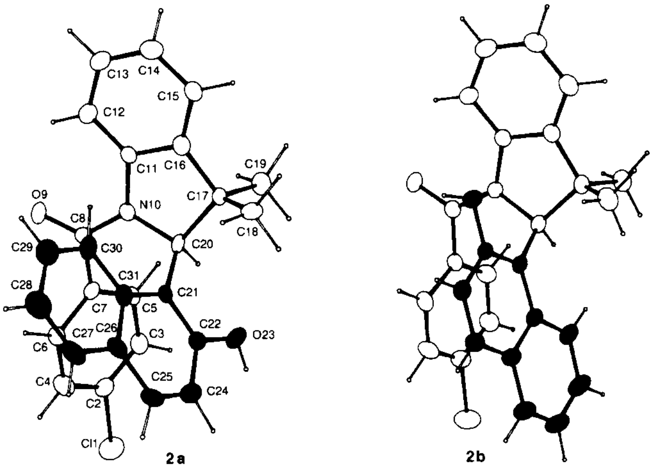


Figure 2 ORTEP Drawing of 2a and 2b

Table 3

Bond Angles (°) of **2a** and **2b** for Non-hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

			2a		**2b**
			Molecule 1	Molecule 2	
Cl(1)	-C(2)	-C(3)	116.9(09)	118.2(08)	119.8(05)
Cl(1)	-C(2)	-C(4)	120.3(11)	119.7(09)	118.2(05)
C(3)	-C(2)	-C(4)	122.8(11)	122.0(12)	122.0(06)
C(2)	-C(3)	-C(5)	118.5(10)	119.1(10)	119.3(05)
C(2)	-C(4)	-C(6)	119.3(13)	117.7(11)	118.2(06)
C(3)	-C(5)	-C(7)	119.2(11)	120.5(10)	120.1(05)
C(4)	-C(6)	-C(7)	120.1(11)	121.7(09)	121.1(05)
C(5)	-C(7)	-C(6)	119.7(09)	118.9(10)	119.2(05)
C(5)	-C(7)	-C(8)	120.8(10)	121.6(09)	121.4(04)
C(6)	-C(7)	-C(8)	119.1(09)	119.4(08)	119.4(04)
C(7)	-C(8)	-O(9)	120.8(09)	119.6(10)	121.3(04)
C(7)	-C(8)	-N(10)	118.4(09)	117.8(09)	117.4(03)
O(9)	-C(8)	-N(10)	120.8(09)	122.5(10)	121.2(04)
C(8)	-N(10)	-C(11)	125.9(08)	124.1(08)	127.2(03)
C(8)	-N(10)	-C(20)	122.9(08)	124.2(08)	122.3(04)
C(11)	-N(10)	-C(20)	110.9(08)	111.2(08)	109.5(03)
N(10)	-C(11)	-C(12)	129.9(09)	130.3(10)	128.7(04)
N(10)	-C(11)	-C(16)	108.8(08)	107.7(09)	110.1(04)
C(12)	-C(11)	-C(16)	121.4(10)	122.0(10)	121.3(05)
C(11)	-C(12)	-C(13)	116.8(10)	117.7(11)	117.1(05)
C(12)	-C(13)	-C(14)	123.6(11)	121.3(11)	121.8(05)
C(13)	-C(14)	-C(15)	117.1(12)	121.7(12)	120.2(06)
C(14)	-C(15)	-C(16)	121.6(11)	118.5(11)	119.1(05)
C(11)	-C(16)	-C(15)	119.4(10)	119.0(10)	120.5(04)
C(11)	-C(16)	-C(17)	113.0(09)	111.9(09)	111.5(04)
C(15)	-C(16)	-C(17)	127.6(10)	129.0(10)	128.0(04)
C(16)	-C(17)	-C(18)	114.0(08)	113.7(10)	111.8(05)
C(16)	-C(17)	-C(19)	109.2(11)	108.1(08)	110.0(04)
C(16)	-C(17)	-C(20)	102.4(09)	102.9(08)	102.6(03)
C(18)	-C(17)	-C(19)	110.5(10)	109.3(09)	110.0(05)
C(18)	-C(17)	-C(20)	113.6(11)	113.8(08)	113.0(04)
C(19)	-C(17)	-C(20)	106.6(09)	108.7(10)	109.2(05)
N(10)	-C(20)	-C(17)	104.2(08)	103.7(07)	103.8(03)
N(10)	-C(20)	-C(21)	114.9(09)	114.2(07)	111.2(03)
C(17)	-C(20)	-C(21)	116.8(08)	118.1(09)	118.0(03)
C(20)	-C(21)	-C(22)	116.4(09)	113.8(09)	121.3(04)
C(20)	-C(21)	-C(31)	124.7(09)	125.6(08)	120.2(04)
C(22)	-C(21)	-C(31)	118.9(10)	120.6(08)	118.4(04)
C(21)	-C(22)	-O(23)	118.1(10)	119.8(08)	119.5(04)
C(21)	-C(22)	-C(24)	121.3(10)	121.2(10)	122.1(04)
O(23)	-C(22)	-C(24)	120.6(08)	119.1(09)	118.4(04)
C(22)	-C(24)	-C(25)	120.1(10)	120.4(10)	119.4(04)
C(24)	-C(25)	-C(26)	121.6(12)	119.9(09)	121.3(04)
C(25)	-C(26)	-C(27)	120.9(11)	119.8(09)	120.7(05)
C(25)	-C(26)	-C(31)	119.1(10)	120.5(10)	119.2(04)
C(27)	-C(26)	-C(31)	120.0(09)	119.6(10)	120.0(05)
C(26)	-C(27)	-C(28)	121.5(12)	121.2(10)	120.1(05)
C(27)	-C(28)	-C(29)	119.8(11)	118.0(11)	121.0(05)
C(28)	-C(29)	-C(30)	121.3(11)	122.4(12)	120.4(06)
C(29)	-C(30)	-C(31)	121.0(12)	121.1(09)	121.3(05)
C(21)	-C(31)	-C(26)	119.0(09)	117.5(09)	119.6(04)
C(21)	-C(31)	-C(30)	124.8(10)	124.9(08)	123.3(04)
C(26)	-C(31)	-C(30)	116.3(09)	117.6(09)	117.1(04)

C(20) bond lengths (**2a**, 1.568 Å, **2b**, 1.565 Å) and the N(10)-C(20) bond lengths (**2a**, 1.495 Å, **2b**, 1.503 Å) are longer than the normal values. These elongation might be due to steric interactions of the naphthyl group with the *cis*-oriented methyl group and the *p*-chlorobenzoyl group respectively. This repulsion may cause the expansion of the C(16)-C(17)-C(18) and C(20)-C(17)-C(18) angles (**2a**, 113.9° and 113.7°, **2b**, 111.8° and 113.0°).

The C(20)-C(21)-C(31) and C(20)-C(21)-C(22) angles are also distorted, which are 125.2° and 115.1° in **2a**. These values seem to indicate the presence of steric repulsion between the naphthyl group and indoline ring.

The deviations of individual atoms from the best plane defined by the phenyl ring carbons of indoline moiety were shown in Table 4.

Table 4

Displacement from Best Plane

	2a		**2b**
	Molecule 1	Molecule 2	
Atoms forming best plane and distances (Å)			
C(11)	-0.016	0.003	0.001
C(12)	0.011	0.001	0.006
C(13)	0.009	-0.006	-0.011
C(14)	-0.024	0.005	0.003
C(15)	0.009	0.001	0.007
C(16)	0.010	0.004	-0.006
Atoms not forming best plane and distances (Å)			
C(5)	-1.549	-0.736	-1.080
C(6)	0.476	1.311	1.158
C(7)	-0.356	0.162	-0.002
C(8)	-0.069	-0.031	-0.067
O(9)	0.149	-0.186	-0.085
N(10)	-0.057	-0.021	-0.025
C(17)	-0.040	0.058	0.002
C(20)	0.064	-0.219	-0.271
H-C(12)	0.035	0.064	0.055
Interatomic Distances (Å)			
O(9)••H–C(12)	2.30	2.29	2.30

The atoms C(10), C(8), O(9) and C(7) are approximately coplanar but C(5) and C(6) are not on this plane. Therefore, the *p*-orbitals of the amide carbonyl group are conjugated not with the *p*-chloropheny group but with the phenyl group of indoline moiety. Of interest, the orientation of the *p*-chlorophenyl group is *trans* with respect to the phenyl moiety of the indoline ring. Therefore, nonbonded O(9)••H-C(12) distances are very close (*ca.* 2.3 Å). In solution, similar geometrical features were observed.

In the pmr spectra, C(12) protons which locate at the effective deshielding zone of the amide carbonyl group resonates at *ca.* 8.2 ppm as a characteristic low-field shifted signal.

The crystal structures of two isomeric compounds have some short interatomic nonbonded contacts. Intermolecular distances between heavy atoms closer than 3.6 Å are collected in Table 5 and the crystal packing is illustrated in Figure 3. Of those, the intermolecular distances between O(9) and O(23') are very close (2.67-2.70 Å), making hydrogen bonding between the amide oxygen and phenolic hydrogen. The two conformations are considered to be firmly frozen in crystalline states by the intermolecular hydrogen bonding. However, the hydrogen bonding is not dominant force for the existence of the atropisomers in solution because the pmr spectral data showed quite different spectral patterns at room temperature.

Table 5

Interatomic Distances (Å) closer than 3.6Å in Crystal [a]

2a

C(6)	O(23'$^{\mathrm{I}}$)	3.50	C(8)	C(4'$^{\mathrm{II}}$)	3.38
C(8)	O(23'$^{\mathrm{III}}$)	3.58	O(9)	C(4'$^{\mathrm{II}}$)	3.28
O(9)	C(22'$^{\mathrm{III}}$)	3.37	O(9)	O(23'$^{\mathrm{III}}$)	2.67
O(9)	O(22'$^{\mathrm{III}}$)	3.24	C(11)	C(6'$^{\mathrm{II}}$)	3.55
C(18)	O(9'$^{\mathrm{II}}$)	3.47	C(22)	O(9'$^{\mathrm{IV}}$)	3.36
O(23)	C(5'$^{\mathrm{IV}}$)	3.59	O(23)	O(9'$^{\mathrm{IV}}$)	2.70
C(24)	O(9'$^{\mathrm{IV}}$)	3.21	C(4')	C(8$^{\mathrm{V}}$)	3.38
C(4')	O(9$^{\mathrm{V}}$)	3.28	C(5')	O(23$^{\mathrm{III}}$)	3.59
C(6')	C(11$^{\mathrm{V}}$)	3.55	C(6')	C(12$^{\mathrm{V}}$)	3.57
O(9')	C(18$^{\mathrm{V}}$)	3.47	O(9')	C(22$^{\mathrm{III}}$)	3.36
O(9')	O(23$^{\mathrm{III}}$)	2.70	O(9')	C(24$^{\mathrm{III}}$)	3.21
C(22')	O(9$^{\mathrm{IV}}$)	3.37	O(23')	C(6$^{\mathrm{IV}}$)	3.50
O(23')	C(8$^{\mathrm{IV}}$)	3.58	O(23')	O(9$^{\mathrm{IV}}$)	2.67
C(24')	O(9$^{\mathrm{IV}}$)	3.24			

2b

C(4)	C(14$^{\mathrm{VI}}$)	3.59	C(6)	C(13$^{\mathrm{VI}}$)	3.53
C(6)	C(14$^{\mathrm{VI}}$)	3.54	O(9)	C(19$^{\mathrm{VI}}$)	3.57
C(9)	C(22$^{\mathrm{VII}}$)	3.32	O(9)	O(23$^{\mathrm{VII}}$)	2.67
O(9)	C(24$^{\mathrm{VII}}$)	3.27	C(13)	C(6$^{\mathrm{VI}}$)	3.53
C(14)	C(4$^{\mathrm{VI}}$)	3.59	C(14)	C(6$^{\mathrm{VI}}$)	3.54
C(19)	O(9$^{\mathrm{VII}}$)	3.57	C(22)	O(9$^{\mathrm{VII}}$)	3.32
O(23)	O(9$^{\mathrm{VII}}$)	2.67	C(24)	O(9$^{\mathrm{VII}}$)	3.27
C(25)	C(29$^{\mathrm{VIII}}$)	3.51	C(29)	C(25$^{\mathrm{IX}}$)	3.51

[a] Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x, y, z:

I	1/2-x,	1/2-y,	-1/2-z	II	1/2+x,	3/2-y,	3/2+z
III	1/2-x	1/2+y,	1/2-z	IV	1/2-x,	-1/2+y,	1/2-z
V	-1/2+x,	3/2-y,	1/2+z				
VI	1-x,	-y,	1-z	VII	1-x,	1-y,	1-z
VIII	1/2-x,	1/2+y,	-z	IX	1/2-x,	-1/2+y,	-z

In the pmr spectra of **2a** and **2b**, C(20) methine proton resonates characteristically: the pmr chemical shift of the proton on C(20) of **2a** appeared at 6.22 ppm, downfield from that of **2b** at 5.99 ppm. In **2a**, the proton is located close to the atom O(23) of naphthyl group. Nonbonded distances of O(23)••H-C(20) is 2.08Å, which is *ca.* 0.5Å shorter than the van der Waals contracts. The lower field shift is attributable to the spatial interaction with the phenolic hydroxy group [10], ruling out the anisotropy effect of naphthalene ring current.

As far as we know, there has been no report concerned with the X-ray structure elucidation of a pair of atropisomers. The present study seem to have valuable information for clarification of the mechanics of restricted rotation about Csp^3-Csp^2 bond. Further studies on the synthesis and isolation of new types of atropisomers are in progress.

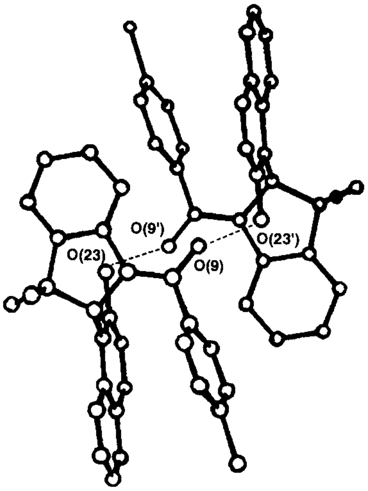


Figure 3 Crystal Packing of 2b

EXPERIMENTAL

Crystal Data for 1-(4'-Chlorobenzoyl)-2-(2''-hydroxynaphthyl)-3,3-dimethylindolines (**2a** and **2b**).

Single crystals of the compounds **2a**,**2b** were prepared by slow evaporation of ethanol-acetone solution. The cell constants were obtained from least squares refinement of the 2θ angle of 20 reflections. The density was measured by flotation in aqueous potassium iodide solution. The crystal data are shown below: **2a**; $C_{27}H_{22}NO_2Cl$, M = 428.0, monoclinic, a = 18.804(14), b = 14.886(12), c = 16.950(15)Å, β = 110.23(6)°, V = 4452(6)$Å^3$, space group $P2_1/n$, Z = 8, Dc = 1.278, Dm = 1.270 gcm^{-3}; **2b**: $C_{27}H_{22}NO_2Cl$, M = 428.0, monoclinic, a = 18.103(13), b = 9.679(7), c = 13.120(9)Å, β = 104.11(5)°, V = 2229(3)$Å^3$, space group $P2_1/a$, Z = 4, Dc = 1.276, Dm = 1.262 gcm^{-3}.

Data Collection and Processing.

Intensity data were collected on RIGAKU AFC-6 automated diffractometer with a graphite monochromated Mo-Kα (0.71069Å) radiation and by using the $2\theta/\omega$-scan mode to a limit of 2θ = 60°. Two reflections were monitored after every measurement of 100 reflections. Of 7201, 6355 independent reflections, 3047, 2795 were treated as observed [$Fo > 3.0\sigma F$, $2\theta < 55°$] for **2a** and **2b** respectively.

The intensities were corrected for Lorentz and polarization effect, but no correction was applied for absorption.

Observed structure factors were converted into normalized structure factor amplitude value (E) by use of a scale factor and the overall temperature factor obtained from Wilson's statistics. The structure was solved by the direct method using the MULTAN78 series of programs. An E map calculated with 500 signed E's (**2a**, E $>$1.27; **2b** $>$1.42), which gave an absolute figure of merit of 1.412 and 1.153 for **2a** and **2b** respectively, revealed the positions of the all expected nonhydrogen atoms. Several further cycles of least-squares refinement of atomic parameters with anisotropic vibrational amplitudes for the nonhydrogen atoms converged to R = 0.12 and 0.11 for **2a** and **2b** respectively. The position of hydrogens bonded to carbon atoms were calculated by using the program HYCO80.

After adding the hydrogens, keeping their vibrational amplitudes fixed (B(H) = B(C)+1.0Å), and refining, we obtained a final R of 0.078 (number of reflections 2756, $2\theta < 55°$, $Fo > 3.0\sigma F$, $Fo > 20.0$) and 0.062 (number of reflections 2444, $2\theta < 55°$, $Fo > 3.0\sigma F$, $Fo > 20.0$) for **2a** and **2b** respectively.

All calculations were performed on the FACOM M-360 computer in the computer center of Kumamoto University with the Universal Crystallographic Computation Program System (UNICS III) [11].

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