Absolute Conformation and Chiroptical Properties. III. Optically Active Methyl *sc*-3-Methyl-3-(substituted 9-triptycyl)butanoate Rotamers[1)]

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(Received January 12, 1994)

Enantiomers of the title rotamers were resolved by the diastereomer method with use of optically active camphorsultam. The absolute conformations about the C_9–C_{alkyl} single bond were determined by the X-ray analysis of one of the diastereomeric amides. All the samples submitted to the X-ray analysis showed their absolute conformation to be *Psc*. Specific rotations of the *Psc* methyl esters of the methyl, methoxy, and chloro compounds at the Na D line were positive, whereas that of the fluoro compound negative. Although the absolute conformation of the methyl compound had been predicted, though not conclusive, to be *Msc* for the dextrorotatory isomer from calculation, it is proved to be *Psc*. Optical rotations and CD spectra were measured and these chiroptical properties were compared with each other. The chiral methyl esters showed similar patterns in CD spectra if their absolute conformations are the same, irrespective of the kinds of substituents in the benzene ring. Features of molecular structures of the triptycene compounds are also compared and the effects of substituents on the structural parameters are discussed.

While separation of chiral rotamers based on restricted rotation about a C_{sp^3}–C_{sp^3} single bond is one of the most interesting topics in stereochemistry, little attention has been focused on the problem due to facile isomerization of the isomers as well as difficulties in separation. The first resolution of enantiomeric rotamers was accomplished in 1975 with use of a dihydroethenoanthracene system **1** carrying a tertiary alkyl group at the 9-position, where the barrier to rotation around the C_9–C_{alkyl} bond was high enough for isolation of the isomers at room temperature (ca. 33 kcal mol^{-1}).[2)] An enantiomeric pair of compound **1** were separated by the diastereomer method, showing optical rotations of the same magnitude but the opposite direction with each other (Chart 1). The absolute conformation of the rotamers was recently established as *Psc* for the dextrorotatory isomer and *Msc* for the levorotatory by the X-ray analysis of one of the (−)-menthyl esters:[3)] This is the first example of the determination of the absolute conformation in this class of rotamers.

We felt that it was important to provide further examples of optical resolution of rotational isomers, because the relationship between the chiroptical properties and molecular structures has not been well-established. Thus we extended this project to triptycene-type compounds, of which stable rotamers have been widely investigated in this laboratory for their reactivities, intramolecular interactions, and so on.[4,5)] Recently, we succeeded in resolving chiral methyl *sc*-3-methyl-3-(1,4-dimethyl- and dimethoxy-9-triptycyl)butanoate rotamers (**2a** and **2b**) by HPLC on an optically active column of triacetylcellulose.[6)] In the paper, the absolute conformation around the C_9–C_{alkyl} bond in these compounds was predicted by comparing calculated CD transitions with observed ones with reservation, because this process contained several ambiguities and the conclusion could be erroneous. Separation of the rotamers

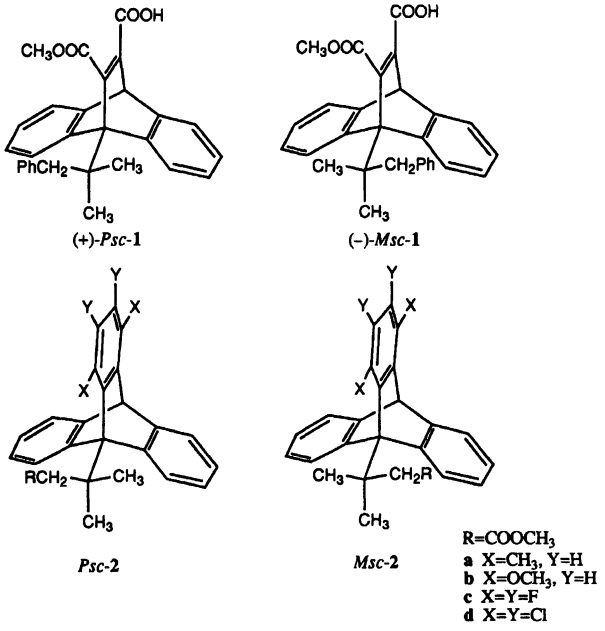


Chart 1.

was possible only in a small scale in the chromatography, which prevented us from further investigation on the optically active isomers. For determination of absolute conformation by experiment it is necessary to obtain the chiral triptycenes in larger quantities. We thus decided to work on separation of chiral isomers in a large scale.

The diastereomer method is known to be convenient for resolution of enantiomers in a preparative scale if one can find a good resolving reagent.[7)] A preliminary experiment revealed that (−)-menthyl ester, which gave a good result for the ethenoanthracene compound (**1**), was insufficient because of poor separation together with difficult crystallization of the chiral triptycene rotamers. Recently (−)-10,2-camphorsultam, (1*S*,5*R*,7*R*)-

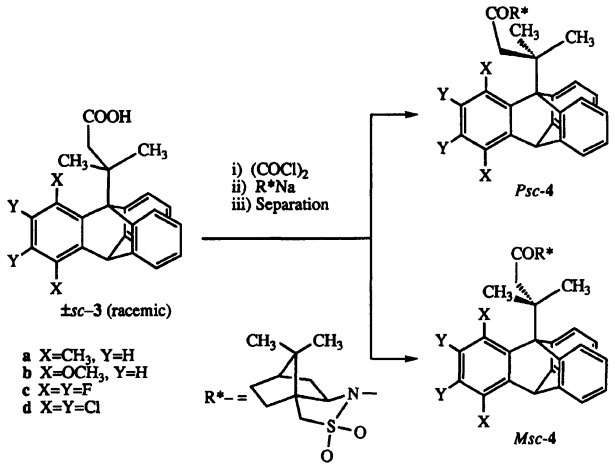
10, 10- dimethyl- 3- thia- 4- azatricyclo[5.2.1.$0^{1,5}$]decane 3,3-dioxide, was found to be an effective reagent for the optical resolution of various carboxylic acids, not only being convenient for separation but also giving good crystals for X-ray analysis.[8—10] The internal reference method, which uses the known absolute configuration in a molecule for X-ray analysis, is one of the most reliable methods for the determination of the absolute stereochemistry.

In this paper, we wish to report the successful optical resolution of four pairs of triptycene rotamers *sc*-**2a**—**d** by the diastereomer method with use of the camphorsultam reagent and the first determination of absolute conformation of the chiral rotamers of triptycene derivatives by X-ray analyses. Optical rotations and CD spectra of the chiral rotamers are compared with each other for correlating the chiroptical properties with the known absolute stereochemistries. Features of molecular structures of the series of compounds are also discussed by comparing the structural parameters. Considerable deformations of the molecules are attributed to steric congestion caused by the 1-substituent at the benzene ring and the 9-substituent, and the interactions of 1-substituents with the 9-alkyl groups, which can be predicted from the structures, are correlated with unusual reactivities in *sc*-rotamers we have reported.[11,12]

Results and Discussion

Optical Resolution. Optical resolution of the triptycene rotamers was performed by the diastereomer method from the racemic *sc*-carboxylic acids (±*sc*-**3**) which were prepared by the known methods.[13,14] The (−)-menthyl esters were found to give difficulty in separation with HPLC as well as difficulty in crystallization. During the exploration of a suitable chiral auxiliary, Harada et al. reported that (−)-10,2-camphorsultam[15] was a very useful auxiliary for optical resolution of racemic carboxylic acids.[8—10] The corresponding amides tend to be easily separated and the separated amides often give crystalline materials. We adopted the camphorsultam reagent for the optical resolution of the triptycene rotamers.

Syntheses of the sultam amides and the subsequent optical resolution were carried out according to the processes shown in Scheme 1. The diastereomeric amides were obtained as a 1 : 1 mixture of diastereomers by treatment of the acid chloride of a racemic carboxylic acid (±*sc*-**3**) with sodium salt of (−)-10,2-camphorsultam, prepared from the camphorsultam and sodium hydride, in a fair yield.[16,17] The diastereomers were found to be much more easily separated by HPLC and/or recrystallization from a suitable solvent than the menthyl esters. A recrystallization of the mixture from hexane-dichloromethane allowed a satisfactory separation for the tetrafluoro compound (**4c**). For the methoxy compound (**4b**), one diastereomer predominantly crystallized from a dichloromethane solution was further purified by recrystallization. The complete separations were attained by HPLC followed by recrystallization for the other compounds, **4a** and **4d**. ^{1}H NMR spectra of the separated compounds indicate that the purity of each diastereomer is more than 99%. All compounds are levorotatory at the Na D line, reflecting a large levorotatory contribution of the camphor moiety.



Scheme 1.

Determination of Absolute Conformation. Molecular structures of one of the diastereomers of compounds **4a**—**4d** were analyzed by X-ray crystallography to determine the absolute conformation about the C_9–C_{alkyl} bond by using the absolute configuration of the camphorsultam group as an internal reference. Crystals of easily eluted diastereomers were submitted for the analysis for **4a** and **4d**, and those of the better and the less soluble diastereomers for **4b** and **4c**, respectively.

The results of X-ray analyses, final atomic coordinates and thermal parameters, are shown in Table 1 and ORTEP drawings in Fig. 1. The structures were solved as the absolute configuration of the camphor moiety was consistent with the known ones, 1*S*,5*R*,7*R*. Selected structural parameters are listed in Tables 2, 3, and 4.

Torsion angles of C(9a)–C(9)–C(17)–C(20) are nearly +60° for all compounds shown in Table 4, indicating that the absolute conformations about the C(9)–C(17) single bond are "*Psc*" for all selected diastereomers. These results assure that the other diastereomer possesses the opposite absolute conformation, namely "*Msc*". Other features of the X-ray structures will be discussed later.

Chiroptical Properties of the Chiral Triptycenes. The separated sultam amides, whose absolute conformations had been determined, were converted to the enantiomeric methyl esters according to the steps shown in Scheme 2. The camphorsultam moiety in the sultam amide was removed under reductive conditions with lithium aluminium hydride to afford an optically active primary alcohol (**5**). This alcohol was oxidized to a carboxylic acid (**3**) with the Jones reagent and the subsequent treatment of the product with di-

Table 1. Atomic Coordinates and Equivalent Isotropic Thermal Parameters in Compounds *Psc*-**4a**—**d**[a)]

Atom	x	y	z	B_{eq}[b)]
		Compoumd *Psc*-**4a**		
S	−0.24579(6)	0.03130(6)	−0.1750(1)	4.82(6)
O(1)	−0.1392(2)	0.1673(3)	−0.3941(4)	11.8(2)
O(2)	−0.2379(2)	0.0547(2)	−0.0449(3)	6.9(1)
O(3)	−0.1995(2)	−0.0307(2)	−0.2120(4)	7.3(1)
N	−0.2258(2)	0.1013(2)	−0.2759(3)	3.67(9)
C(1)	0.0643(3)	−0.0232(2)	−0.2477(5)	5.4(1)
C(2)	0.0970(4)	−0.0924(3)	−0.2413(8)	7.7(2)
C(3)	0.1505(5)	−0.1132(3)	−0.1510(11)	8.8(3)
C(4)	0.1804(3)	−0.0652(3)	−0.0582(6)	7.0(2)
C(4a)	0.1488(2)	0.0062(2)	−0.0634(5)	4.8(1)
C(5)	0.0918(5)	0.0832(4)	0.2339(5)	7.1(2)
C(6)	0.0248(6)	0.1066(4)	0.2896(6)	7.7(2)
C(7)	−0.0370(5)	0.1357(3)	0.2172(6)	6.6(2)
C(8)	−0.0301(3)	0.1379(2)	0.0784(4)	4.6(1)
C(8a)	0.0397(2)	0.1131(2)	0.0203(3)	3.4(1)
C(9)	0.0633(2)	0.1112(2)	−0.1272(3)	2.8(1)
C(9a)	0.0898(2)	0.0286(2)	−0.1525(4)	3.6(1)
C(10)	0.1754(3)	0.0632(3)	0.0301(5)	5.5(1)
C(10a)	0.1014(3)	0.0876(2)	0.1019(4)	4.8(1)
C(11)	0.2039(2)	0.1292(2)	−0.0486(4)	4.6(1)
C(12)	0.1448(2)	0.1550(2)	−0.1311(4)	3.6(1)
C(13)	0.1644(3)	0.2174(3)	−0.2017(5)	4.7(1)
C(14)	0.2404(3)	0.2494(3)	−0.1913(6)	6.2(2)
C(15)	0.2981(4)	0.2193(4)	−0.1105(7)	7.5(2)
C(16)	0.2798(3)	0.1591(4)	−0.0371(6)	7.0(2)
C(17)	−0.0018(2)	0.1461(2)	−0.2188(4)	3.8(1)
C(18)	0.0318(3)	0.1480(4)	−0.3612(5)	5.4(2)
C(19)	−0.0206(3)	0.2265(3)	−0.1781(6)	5.7(2)
C(20)	−0.0822(2)	0.1034(3)	−0.2076(5)	5.0(1)
C(21)	−0.1485(2)	0.1257(3)	−0.3019(5)	5.9(2)
C(22)	−0.3478(3)	0.0206(3)	−0.2277(7)	6.9(2)
C(23)	−0.3701(2)	0.0847(2)	−0.3100(4)	3.8(1)
C(24)	−0.2919(2)	0.1145(2)	−0.3693(4)	3.8(1)
C(25)	−0.3131(3)	0.1953(3)	−0.3971(7)	6.2(2)
C(26)	−0.4039(3)	0.1956(3)	−0.3728(6)	5.7(2)
C(27)	−0.4447(3)	0.1478(3)	−0.4751(5)	5.7(2)
C(28)	−0.4262(3)	0.0705(3)	−0.4256(6)	5.4(2)
C(29)	−0.4106(3)	0.1521(3)	−0.2474(5)	5.5(2)
C(30)	−0.3686(5)	0.1832(7)	−0.1269(10)	9.4(3)
C(31)	−0.4981(4)	0.1383(7)	−0.2056(8)	10.1(3)
C(32)	0.0054(5)	−0.0153(5)	−0.3653(7)	9.5(3)
C(33)	0.2422(6)	−0.0879(5)	0.0414(14)	12.2(4)
		Compoumd *Psc*-**4b**		
S	0.56309(9)	0.04247(9)	0.38569(4)	3.82(3)
O(1)	0.3211(2)	0.2795(2)	0.4118(1)	4.12(8)
O(2)	0.5565(3)	0.0065(3)	0.4352(1)	6.3(1)
O(3)	0.5317(3)	−0.0472(3)	0.3502(2)	6.0(1)
O(4)	0.0655(3)	0.1582(2)	0.4466(1)	4.69(8)
O(5)	−0.2368(3)	−0.2507(3)	0.4562(1)	5.26(9)
N	0.4749(3)	0.1707(2)	0.3776(1)	2.95(7)
C(1)	−0.0083(3)	0.0569(3)	0.4488(1)	3.01(8)
C(2)	−0.0931(4)	0.0437(4)	0.4869(1)	4.0(1)
C(3)	−0.1696(4)	−0.0550(4)	0.4915(2)	4.1(1)
C(4)	−0.1641(4)	−0.1474(4)	0.4576(2)	3.7(1)
C(4a)	−0.0809(3)	−0.1353(3)	0.4194(1)	2.84(9)
C(5)	0.0941(4)	−0.3973(3)	0.3831(2)	3.7(1)
C(6)	0.2180(4)	−0.4284(4)	0.3801(2)	4.2(1)
C(7)	0.3027(4)	−0.3374(4)	0.3716(2)	4.1(1)

Table1. (Continued)

Atom	x	y	z	B_{eq}[b)]
C(8)	0.2677(4)	−0.2145(3)	0.3664(1)	3.2(1)
C(8a)	0.1438(3)	−0.1813(3)	0.3703(1)	2.62(8)
C(9)	0.0845(3)	−0.0488(3)	0.3660(1)	2.44(8)
C(9a)	0.0005(3)	−0.0360(3)	0.4137(1)	2.50(7)
C(10)	−0.0738(3)	−0.2322(3)	0.3795(1)	3.17(9)
C(10a)	0.0588(3)	−0.2751(3)	0.3784(1)	2.78(8)
C(11)	−0.0952(3)	−0.1644(3)	0.3325(1)	3.08(9)
C(12)	−0.0128(3)	−0.0680(3)	0.3242(1)	2.74(8)
C(13)	−0.0251(4)	−0.0016(4)	0.2809(1)	3.5(1)
C(14)	−0.1211(5)	−0.0322(5)	0.2479(2)	4.7(1)
C(15)	−0.2023(5)	−0.1253(5)	0.2584(2)	5.0(1)
C(16)	−0.1903(4)	−0.1924(4)	0.3007(2)	4.2(1)
C(17)	0.1785(3)	0.0591(3)	0.3555(1)	2.58(8)
C(18)	0.1062(4)	0.1821(4)	0.3492(2)	3.4(1)
C(19)	0.2539(4)	0.0378(4)	0.3087(2)	3.3(1)
C(20)	0.2747(3)	0.0664(3)	0.3986(1)	2.99(9)
C(21)	0.3552(3)	0.1783(3)	0.3974(1)	2.90(9)
C(22)	0.7081(4)	0.1156(4)	0.3721(2)	3.9(1)
C(23)	0.6806(3)	0.2484(3)	0.3591(2)	3.5(1)
C(24)	0.5513(3)	0.2824(3)	0.3789(2)	3.4(1)
C(25)	0.5094(4)	0.3878(4)	0.3444(2)	4.8(1)
C(26)	0.6276(4)	0.4153(4)	0.3156(2)	5.2(1)
C(27)	0.7251(5)	0.4640(4)	0.3514(3)	6.5(2)
C(28)	0.7672(5)	0.3469(5)	0.3798(2)	5.4(1)
C(29)	0.6747(4)	0.2840(4)	0.3046(2)	4.1(1)
C(30)	0.5867(5)	0.2065(6)	0.2729(2)	5.4(2)
C(31)	0.8023(5)	0.2815(5)	0.2797(2)	5.6(2)
C(32)	0.0451(7)	0.2625(5)	0.4756(2)	6.8(2)
C(33)	−0.3307(7)	−0.2597(7)	0.4931(3)	7.5(2)
		Compound *Psc*-**4c**		
S	0.71450(8)	0.49979(3)	0.1183(1)	4.09(2)
F(1)	0.6244(2)	0.66279(7)	−0.0397(2)	4.42(6)
F(2)	0.7778(2)	0.72786(8)	0.0339(3)	5.47(7)
F(3)	0.7462(2)	0.77823(8)	0.2670(3)	6.56(8)
F(4)	0.5430(2)	0.75685(8)	0.4249(2)	5.47(7)
O(1)	0.4800(4)	0.52118(9)	−0.1598(3)	5.85(9)
O(2)	0.6636(3)	0.5044(1)	0.2506(3)	5.19(8)
O(3)	0.7929(3)	0.5367(1)	0.0713(4)	6.07(9)
N	0.5942(3)	0.49030(9)	0.0080(3)	3.13(7)
C(1)	0.5954(3)	0.6826(1)	0.0794(4)	3.16(8)
C(2)	0.6795(3)	0.7178(1)	0.1153(4)	3.8(1)
C(3)	0.6643(4)	0.7422(1)	0.2322(4)	4.2(1)
C(4)	0.5605(4)	0.7326(1)	0.3102(4)	3.7(1)
C(4a)	0.4750(3)	0.6985(1)	0.2741(3)	2.98(8)
C(5)	0.3590(4)	0.6207(2)	0.5202(4)	4.0(1)
C(6)	0.3699(4)	0.5729(2)	0.5444(4)	4.4(1)
C(7)	0.3878(4)	0.5437(1)	0.4397(4)	4.2(1)
C(8)	0.3924(4)	0.5594(1)	0.3070(4)	3.7(1)
C(8a)	0.3811(3)	0.6074(1)	0.2808(3)	3.02(8)
C(9)	0.3828(3)	0.6331(1)	0.1410(3)	2.75(8)
C(9a)	0.4915(3)	0.6710(1)	0.1576(3)	2.66(8)
C(10)	0.3555(4)	0.6880(1)	0.3517(4)	3.34(9)
C(10a)	0.3640(3)	0.6369(1)	0.3902(4)	3.25(9)
C(11)	0.2491(3)	0.6928(1)	0.2522(4)	3.19(9)
C(12)	0.2596(3)	0.6631(1)	0.1411(3)	2.97(8)
C(13)	0.1635(4)	0.6639(1)	0.0458(4)	3.8(1)
C(14)	0.0610(4)	0.6944(2)	0.0610(4)	4.3(1)
C(15)	0.0541(4)	0.7246(2)	0.1682(4)	4.4(1)
C(16)	0.1482(4)	0.7234(1)	0.2670(4)	4.0(1)
C(17)	0.3949(4)	0.5990(1)	0.0166(3)	3.22(9)

Table1. (Continued)

Atom	x	y	z	B_{eq} [b]
C(18)	0.3907(5)	0.6266(1)	−0.1181(4)	3.8(1)
C(19)	0.2830(5)	0.5635(2)	0.0202(5)	4.5(1)
C(20)	0.5242(4)	0.5724(1)	0.0262(4)	3.7(1)
C(21)	0.5297(4)	0.5271(1)	−0.0513(4)	3.8(1)
C(22)	0.7880(4)	0.4441(2)	0.0947(7)	5.6(1)
C(23)	0.6941(3)	0.4138(1)	0.0201(4)	3.9(1)
C(24)	0.6083(3)	0.4456(1)	−0.0664(4)	3.25(9)
C(25)	0.4876(4)	0.4163(1)	−0.0869(5)	4.0(1)
C(26)	0.5274(4)	0.3690(1)	−0.0288(5)	4.4(1)
C(27)	0.6316(5)	0.3488(2)	−0.1168(6)	5.7(1)
C(28)	0.7492(4)	0.3781(2)	−0.0804(6)	5.7(1)
C(29)	0.5972(4)	0.3835(1)	0.1013(4)	4.5(1)
C(30)	0.5118(6)	0.4090(2)	0.2034(6)	6.1(2)
C(31)	0.6616(8)	0.3420(2)	0.1748(7)	8.2(2)
		Compound *Psc*-**4d**		
Cl(1)	0.0000	0.0000	0.0000	3.98(3)
Cl(2)	−0.2358(1)	−0.1187(1)	−0.1385(1)	3.99(2)
Cl(3)	−0.3714(1)	−0.1855(1)	0.0735(1)	4.05(2)
Cl(4)	−0.2674(1)	−0.1216(1)	0.4508(1)	4.41(3)
S	0.1354(2)	0.5159(1)	0.2855(2)	3.84(3)
O(1)	0.1762(3)	0.1600(3)	−0.0020(3)	4.54(8)
O(2)	−0.0228(3)	0.5732(3)	0.2133(4)	7.2(1)
O(3)	0.1776(4)	0.5095(3)	0.4527(4)	7.1(1)
N	0.2241(3)	0.3476(3)	0.1745(3)	2.86(7)
C(1)	−0.0668(4)	−0.0223(3)	0.1419(4)	2.62(8)
C(2)	−0.1774(4)	−0.0810(4)	0.0717(4)	2.64(8)
C(3)	−0.2379(4)	−0.1119(4)	0.1641(4)	2.75(8)
C(4)	−0.1931(4)	−0.0805(4)	0.3312(4)	2.88(9)
C(4a)	−0.0853(4)	−0.0210(4)	0.4020(4)	2.44(8)
C(5)	−0.1498(5)	0.2736(5)	0.7415(5)	3.9(1)
C(6)	−0.1670(6)	0.4170(6)	0.7783(6)	4.9(1)
C(7)	−0.0969(5)	0.4545(5)	0.7036(6)	4.9(1)
C(8)	−0.0054(5)	0.3518(4)	0.5907(5)	3.9(1)
C(8a)	0.0120(4)	0.2070(4)	0.5508(4)	3.00(8)
C(9)	0.1058(4)	0.0742(4)	0.4276(4)	2.27(7)
C(9a)	−0.0170(4)	0.0104(3)	0.3114(4)	2.27(8)
C(10)	−0.0318(4)	0.0127(4)	0.5850(4)	3.00(9)
C(10a)	−0.0588(4)	0.1702(4)	0.6299(4)	3.12(8)
C(11)	0.1386(3)	−0.0778(3)	0.6113(4)	2.89(8)
C(12)	0.2147(4)	−0.0472(3)	0.5329(4)	2.65(8)
C(13)	0.3710(4)	−0.1264(4)	0.5538(4)	2.82(9)
C(14)	0.4478(4)	−0.2346(4)	0.6442(4)	3.6(1)
C(15)	0.3696(5)	−0.2666(4)	0.7159(5)	3.9(1)
C(16)	0.2128(4)	−0.1868(4)	0.7001(4)	3.27(9)
C(17)	0.1996(4)	0.1071(4)	0.3458(4)	2.87(8)
C(18)	0.2956(5)	−0.0352(4)	0.2369(5)	3.8(1)
C(19)	0.3149(5)	0.1661(5)	0.4815(5)	4.2(1)
C(20)	0.0932(5)	0.2332(4)	0.2488(5)	3.1(1)
C(21)	0.1632(4)	0.2424(4)	0.1285(5)	3.0(1)
C(22)	0.2289(5)	0.6026(4)	0.2416(6)	4.5(1)
C(23)	0.3312(4)	0.4885(4)	0.1234(4)	3.33(9)
C(24)	0.2805(4)	0.3590(4)	0.0485(4)	3.19(9)
C(25)	0.4274(5)	0.2284(4)	−0.0002(5)	4.4(1)
C(26)	0.5339(5)	0.3023(4)	0.0267(5)	4.7(1)
C(27)	0.4628(6)	0.4026(5)	−0.0979(6)	5.5(1)
C(28)	0.3250(6)	0.5345(6)	−0.0277(6)	5.1(1)
C(29)	0.5047(4)	0.4134(4)	0.1901(5)	3.8(1)
C(30)	0.5875(6)	0.5161(6)	0.2397(7)	6.3(2)
C(31)	0.5497(6)	0.3428(6)	0.3372(6)	6.2(1)

a) Values in parentheses are estimated standard deviations. b) $B_{eq}/\text{Å}^2=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

azomethane gave a chiral methyl ester.

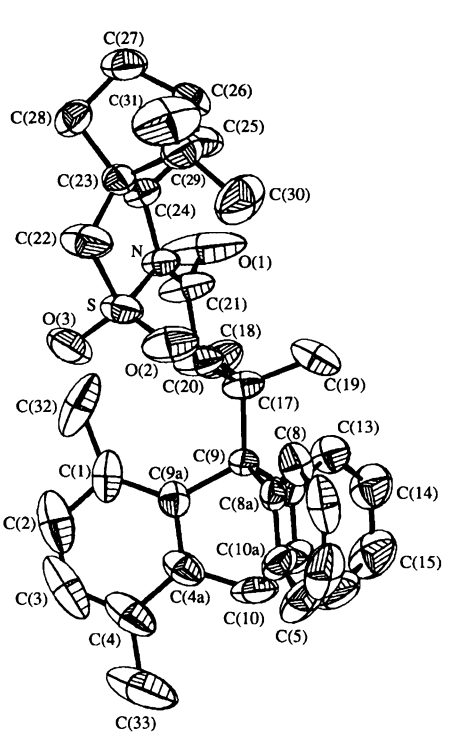
The barrier to rotation about the C_9–C_{alkyl} bond is so high (>35 kcal mol^{-1})[4] that no isomerization takes place under these reaction conditions. Therefore the optical purities of the methyl esters should be equal to the purities of the corresponding diastereomeric amides. Indeed optical purities of the methyl esters were better than 99% as checked by NMR measurements with a chiral shift reagent. When a small amount of shift reagent was added to a chloroform-*d* solution of a chiral methyl ester, only one set of NMR signals were observed, whereas the racemic mixture of the methyl ester showed well separated two sets of signals under the same conditions.

Specific rotations of the *Psc* methyl esters were measured at the Na D line in chloroform and the values are listed in Table 5. In every compound, a pair of enantiomers have rotations with opposite directions and identical absolute values. The signs of rotations are positive for the *Psc*-isomers and negative for *Msc*-isomers except for the tetrafluoro compound, of which signs of rotation are vice versa even though the magnitudes of rotation were very small.

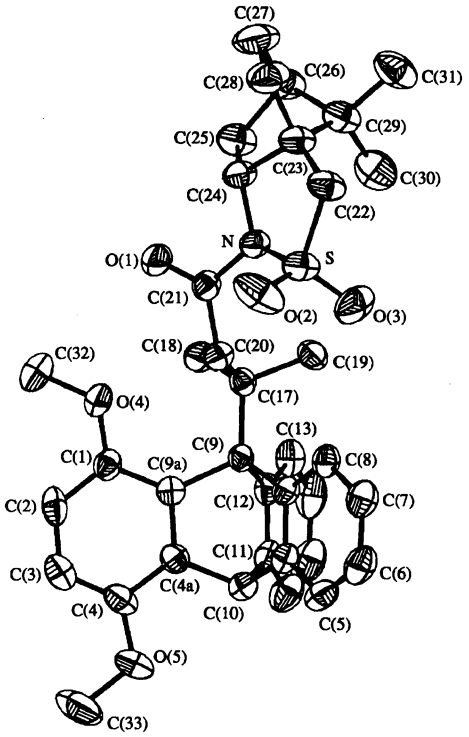
The intermediate chiral compounds, the primary alcohols (**5**) and carboxylic acids (**3**), show specific rotations with the same sign as that of the corresponding methyl ester if the absolute conformations are the same, shown in Table 5. We also notice that the chiral carboxylic acids show almost the same degree of rotation as the methyl esters, whereas the alcohols, which lack carbonyl groups, do smaller values than others but for the tetrafluoro compounds. These tendencies mean that the chiral environment of the triptycene framework itself is a dominant factor for determining the direction of rotations and the substituent attached to the 9-*t*-alkyl group influences the magnitude of rotations only moderately.

As mentioned above, the tetrafluoro compounds showed different tendencies in their optical rotations compared with the other compounds. Although it is difficult to elucidate the exceptional tendencies of the tetrafluoro compounds from available data, the strongly electron-withdrawing properties of fluorine atoms attached to the benzene ring will influence the optical rotations because of the electronic structures of the compounds concerned. The electronic structures should be better reflected by the CD spectra. Thus we measured the CD spectra of the *Psc*-methyl esters for methanol solutions and the results are shown in Fig. 2.

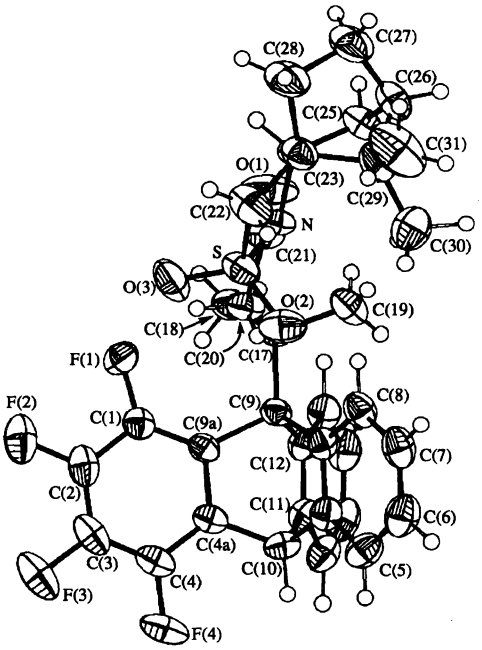
Relatively strong peaks were observed in the range of 200—270 nm, whose $\Delta\varepsilon$ values are ±10 at the most, and weak peaks in the longer wavelength region. These peaks correspond to UV absorptions; a strong band at ca. 214 nm (K band) and some weak bands in 260—280 nm range (B band).[6] Although it is outside of our interest for the time being to assign each CD signal, the chromophores of the three benzene rings (π–π^*) and



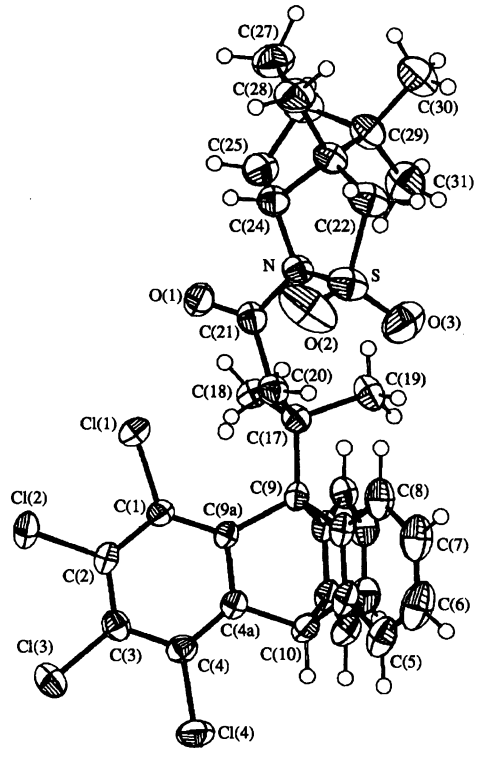
Psc-**4a**



Psc-**4b**



Psc-**4c**



Psc-**4d**

Fig. 1. ORTEP drawings of compounds *Psc*-**4a**—**d** with thermal ellipsoids with 50% probabilities (hydrogen atoms are omitted for *Psc*-**4a** and *Psc*-**4b**).

carbonyl group (n–π^* and π–π^*) should play important roles in the CD spectra.

Comparing these spectra, one notices that all compounds have a similar pattern regardless of kinds of the substituents at positions 1 through 4 if minor changes are neglected. Namely, each compound has following

Table 2. Selected Bond Distances and Nonbonding Distances (Å) in Compounds *Psc*-**4a**—**d**[a)]

Compound	*Psc*-**4a**	*Psc*-**4b**	*Psc*-**4c**	*Psc*-**4d**
C(9)–C(8a)	1.571(5)	1.580(5)	1.577(4)	1.575(4)
C(9)–C(9a)	1.599(5)	1.605(5)	1.587(4)	1.609(4)
C(9)–C(12)	1.569(5)	1.578(5)	1.556(5)	1.589(4)
C(9)–C(17)	1.569(5)	1.580(5)	1.584(4)	1.578(4)
C(10)–C(4a)	1.489(7)	1.525(5)	1.509(5)	1.514(4)
C(10)–C(10a)	1.499(7)	1.512(5)	1.512(5)	1.494(5)
C(10)–C(11)	1.518(7)	1.508(5)	1.504(5)	1.508(4)
C(17)–C(18)	1.571(6)	1.558(5)	1.558(5)	1.556(5)
C(17)–C(19)	1.566(7)	1.547(5)	1.557(6)	1.582(5)
C(17)–C(20)	1.548(6)	1.584(5)	1.565(6)	1.574(5)
C(20)–C(21)	1.522(6)	1.497(5)	1.509(5)	1.511(5)
C(21)–O(1)	1.228(7)	1.225(4)	1.214(5)	1.204(4)
C(21)–N	1.380(5)	1.410(4)	1.386(4)	1.411(4)
C(1)–X[b)]	1.563(9)	1.364(4)	1.351(4)	1.734(3)
C(4)–Y[c)]	1.507(10)	1.372(5)	1.351(4)	1.740(3)
C(18),X	3.028(10)	2.733(6)	2.786(5)	2.998(4)
C(20),X	3.079(10)	2.808(5)	2.871(4)	3.032(4)

a) Values in parentheses are estimated standard deviations. b) The first atom in the substituent at C(1). c) The first atom in the substituent at C(4).

Table 3. Selected Bond Angles (°) in Compounds *Psc*-**4a**—**d**[a)]

Compound	*Psc*-**4a**	*Psc*-**4b**	*Psc*-**4c**	*Psc*-**4d**
C(9a)–C(1)–X[b)]	131.0(5)	120.6(3)	125.0(3)	125.0(2)
C(4a)–C(4)–Y[c)]	122.3(6)	115.3(3)	119.7(3)	120.8(3)
C(8a)–C(9)–C(17)	113.8(3)	115.2(2)	113.8(2)	115.7(3)
C(9a)–C(9)–C(17)	118.4(3)	116.8(3)	116.4(3)	118.5(2)
C(12)–C(9)–C(17)	111.4(3)	113.3(3)	114.0(3)	111.5(3)
C(8a)–C(9)–C(9a)	104.3(3)	104.4(3)	103.6(2)	103.3(2)
C(8a)–C(9)–C(12)	103.1(3)	101.9(2)	104.4(2)	103.8(2)
C(9a)–C(9)–C(12)	104.3(3)	103.4(2)	103.1(2)	102.2(2)
C(4a)–C(10)–C(10a)	106.7(4)	106.0(3)	105.8(3)	105.9(3)
C(4a)–C(10)–C(11)	107.2(4)	106.0(3)	105.4(3)	104.0(2)
C(10a)–C(10)–C(11)	106.4(4)	106.2(3)	107.5(3)	107.9(3)
C(9)–C(17)–C(18)	109.3(3)	109.3(3)	111.1(3)	110.4(3)
C(9)–C(17)–C(19)	111.1(3)	112.6(3)	108.8(3)	110.0(3)
C(9)–C(17)–C(20)	109.7(3)	109.0(3)	108.8(3)	111.7(3)
C(18)–C(17)–C(19)	107.5(4)	107.5(3)	109.1(3)	107.5(3)
C(18)–C(17)–C(20)	112.6(4)	111.8(3)	108.9(3)	112.0(3)
C(19)–C(17)–C(20)	106.6(4)	106.6(3)	110.0(3)	104.9(3)
C(17)–C(20)–C(21)	115.8(4)	114.1(3)	114.8(3)	115.0(3)

a) Values in parentheses are estimated standard deviations. b) The first atom in the substituent at C(1). c) The first atom in the substituent at C(4).

peaks in common; a broad positive band at around 250—260 nm, a broad negative band at around 230—240 nm, relatively sharp peaks at 220 and 200 nm, and a trough at 210 nm. For the CD spectrum the tetrafluoro compound (*Psc*-**2c**) is not an exception, though it is so in the specific rotations. There seems to be a certain correlation between the chiroptical data and the absolute conformation: If the absolute conformations are the same, the chiral triptycenes show similar CD patterns.

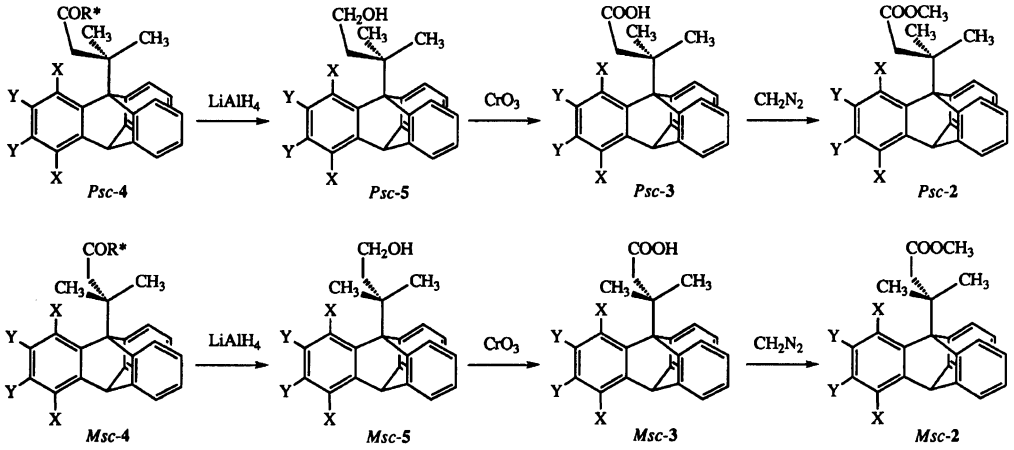
From the CD spectra, we judge that the opposite rotation of the fluoro compound to others at the Na D line happened due to the fortuitous deviation of the weak interactions with the polarized light, as the CD spectra deviate at longer wavelength region above and below the 0° line.

Although we feel it is premature to propose the empirical rule in general for various triptycene derivatives, it will be worthwhile to discuss the structural features and the CD spectra here. Since the only difference in the enantiomers discussed here is the placement of the methoxycarbonyl group either in the right-hand side or

Table 4. Selected Torsion and Dihedral Angles (°) in Compounds *Psc*-**4a**—**d**

Compound	*Psc*-**4a**	*Psc*-**4b**	*Psc*-**4c**	*Psc*-**4d**
C(9a)–C(9)–C(17)–C(20)	61.6	62.3	58.2	64.9
C(9)–C(17)–C(20)–C(21)	−173.5	−169.9	158.3	−163.0
C(17)–C(20)–C(21)–O(1)	9.7	79.9	37.3	76.6
C(17)–C(20)–C(21)–N	−165.4	−97.8	−141.5	−99.8
O(1)–C(21)–N–S	166.5	145.1	153.5	145.0
Benzene A–Benzene B[a)]	119.8	123.3	120.6	120.9
Benzene A–Benzene C	122.7	117.9	116.9	115.2
Benzene B–Benzene C	117.3	118.8	122.1	124.0

a) Dihedral angles between average planes comprised of carbon atoms as follows; Benzene A: C(1), C(2), C(3), C(4), C(4a), C(9a); Benzene B: C(5), C(6), C(7), C(8), C(8a), C(10a); Benzene C: C(11)–C(16).



Scheme 2.

Table 5. Specific Rotation, $[\alpha]_D/°$, of Optically Active Compounds **2**, **3**, and **5**[a)]

Compound	*Psc*-**2**	*Msc*-**2**	*Psc*-**3**	*Msc*-**3**	*Psc*-**5**	*Msc*-**5**
a	+32	−32	+17	−17	+27	−27
b	+20	−20	+8.2	−8.8	+20	−21
c	−2.2	+2.2	−6.2	+5.1	−0.7	+1.1
d	+24	−23	+15	−16	+27	−26

a) All values were measured for a chloroform solution at 23—25 °C. Concentrations of the sample (*c*) were 0.3—1.0 g/100 mL (see Experimental).

the left of the triptycene skeleton, it will be natural to consider that the methoxycarbonylmethyl group should play the decisive role in determining the CD spectra. A naive consideration would lead to the prediction that the direction of electronic transition is reversed when the substituted benzeno group is changed from a 1,4-dimethylbenzeno to a 1,2,3,4-tetrafluorobenzeno group. However, the experimental results show that these effects are negligibly small in determining the patterns of the CD spectra. Further experimental work is necessary to elucidate the relationship between the structure and the chiroptical properties.

Comparison of the CD spectra reported in this paper with those reported on the chiral isomer separated by HPLC on triacetylcellulose reveals that the first eluted form was the *Psc* for the dimethyl compound (**2a**), whereas it was the *Msc*-form for the dimethoxy compound (**2b**).[6)] Interestingly the order of elution of the *Psc* and *Msc* enantiomers is different for the two compounds. The absolute conformations of the first elutions had been predicted with some reservations as *Msc* for both the compounds by comparing intensities and signs of the observed CD spectra with the calculated ones for B-type transitions. Therefore the prediction is correct for the methoxy compound, while it is incorrect for the methyl compound. The disagreement in the methyl compound may be caused by immaturity and limitations of the calculation method, which contains several approximations. Furthermore the intensities of transitions are known to be considerably influenced by geometries used for the calculation. Although the X-ray structure as well as MM2 optimized structures was

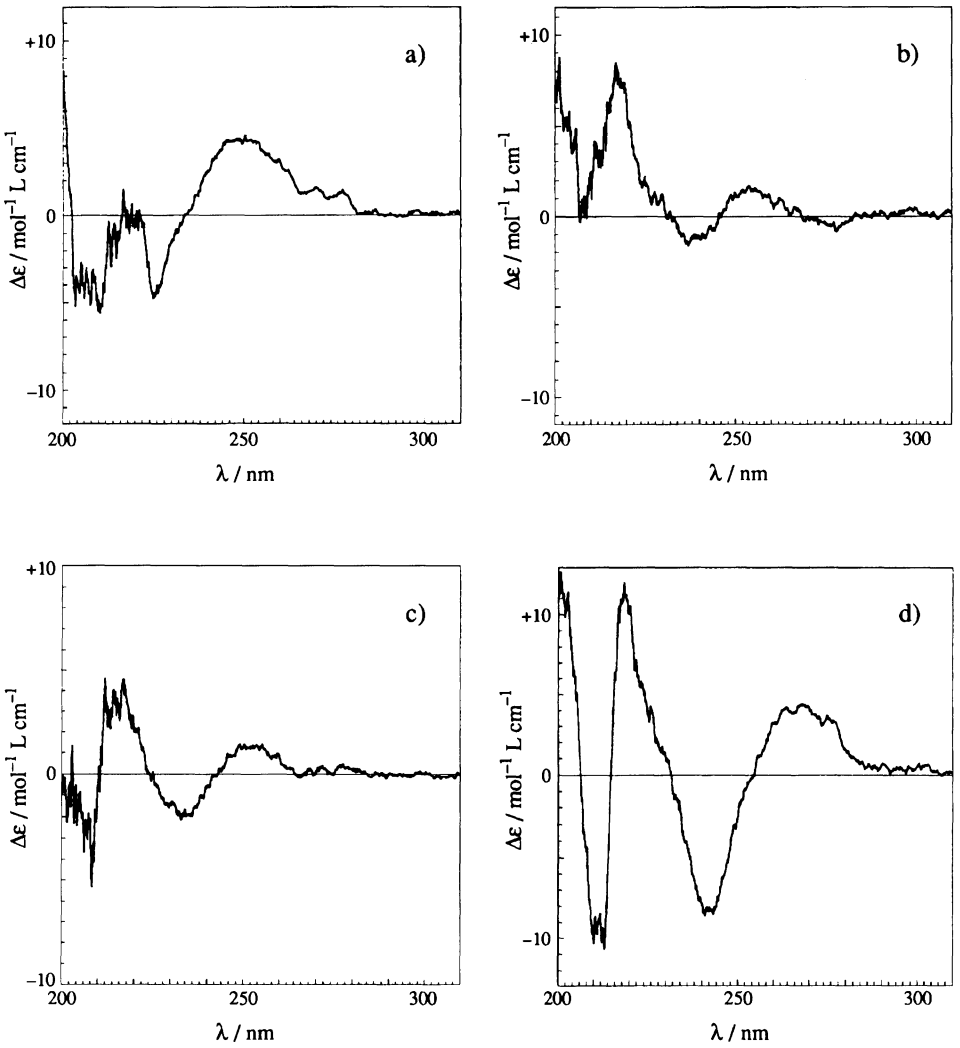


Fig. 2. CD spectra of compounds *Psc*-**2a**—**d** in methanol. a) *Psc*-**2a**, b) *Psc*-**2b**, c) *Psc*-**2c**, d) *Psc*-**2d**.

used for the calculation of the CD spectrum of **2a**, it is possible that a molecule takes a different conformation in solution from those obtained by X-ray analysis and calculations. Further experimental and theoretical studies will be necessary to establish a general rule for correlating the absolute conformations of the chiral triptycenes with their CD spectra.

Features of Molecular Structure. The X-ray structures of the triptycene compounds described above can provide further valuable information other than the absolute conformation because these are the first systematic structural data of a series of triptycene rotamers. Comparison of structural features of the molecules of compounds **4a**—**d** will provide information necessary for discussing the molecular interactions as well as reactivities of rotational isomers.

All compounds possess characteristic structures for triptycenes carrying a tertiary alkyl group at the 9-positions, as were observed for similar triptycene compounds.[6,12,18] The most significant deformations are found at the bonds and angles involving the bridgehead carbon, C(9), that has a tertiary alkyl group. All bond distances connecting the C(9) atom to others are longer than usual values. The C(9)–C(9a) bonds of ca. 1.60 Å are quite long compared to a normal sp^3–sp^2 bond and other three bonds also longer by 0.04—0.07 Å than standard values. Bond angles at C(9) are large outside the triptycene bridge and small inside. The C(9a)–C(9)–C(17) angles are larger by ca. 10° than the regular tetrahedral angle and increase as the substituent at the 1-position becomes bulky. No significant deformations are observed in structural parameters at another bridgehead carbon, C(10), which lacks an attached alkyl group. The large deformations at the C-(9) atom are ascribed to the steric interaction between the tertiary alkyl group at the 9-position and the 1-substituent rather than the formation of triptycene skeleton itself.

Dihedral angles between the three benzene rings are listed in Table 4. All angles are nearly 120° in every compound, suggesting that a deformation such as widening or narrowing the notches between the two benzeno groups is less important in these compounds, being attributed to the similar sizes of the methyl groups

and the substituted methyl groups. The deformations of benzene rings from planarity are also negligible in all compounds. These findings contrast the structures of triptycene derivatives having a small fused ring, where the deviations of benzene rings from planarity are significant.[19]

The carbonyl carbons C(20) are directed toward outside of the triptycene skeleton to avoid the steric interactions. The conformations in the amide moiety in these compounds are different from one to another as can be seen from dihedral angles in Table 4. In *Psc*-**4b** and *Psc*-**4d**, torsion angles of C(17)–C(20)–C(21)–O(1) are about 80°, namely, the oxygen extends toward the substituted benzeno bridge (Benzene A) and the amide-nitrogen toward one of the unsubstituted benzeno bridge (Benzene B). In contrast, the torsion angle becomes as small as 9.7° in the methyl compound (*Psc*-**4a**) and the carbonyl group nearly eclipses the C(17)–C-(20) bond. The conformation in the fluoro compound is in between the two cases. The O(1)–C(21)–N–S angles fall in the range 145—165° in all compounds, suggesting that amide moiety takes an *E* conformation, though not ideal.

The substituent at the 1-position (X) are bent away from the 9-substituent to avoid the steric interactions except for the 1-methoxy group in *Psc*-**4b**. In other compounds, the bond angles of C(9a)–C(1)–X are within the range of 125—131° and the degree of bending increases as the van der Waals radius of the substituent group becomes large, in the order of F<Cl<CH_3. The bending of the 1-methyl group in *Psc*-**4a** is the most significant of them, being attributed to the largest size of the methyl group as well as lack of a substituent at the 2-position which prevents the deformation by the buttressing effects. Similar deformations at the 4-substituents are much less significant than the 1-substituent because there is no substituent at the 10-position which interacts with them.

To make a contrast with these, the C(9a)–C(1)–X bond angle in the methoxy compound is nearly 120°, this angle being anomalous from a viewpoint of the steric interaction and absence of the buttressing effect. A similar phenomenon was observed in triptycenes carrying a five-membered ring fused to the triptycene skeleton.[19] In the paper, we have proposed an attractive interaction, hydrogen bond, between the methoxy-oxygen and hydrogens in the 9-alkyl group located closely to the oxygen atom to explain the structural feature. The unusually high population of the *sc*-isomer in 9-isobutyl-1,4-dimethoxytriptycene compared to an expected one from the steric effects is also attributed to this interaction.[20] We wish to ascribe the exceptional bond angle in the dimethoxy compound again to the CH···O hydrogen bond. The distances between the 1-oxygen and the nearest hydrogens in the 18-methyl and the 20-methylene are only 2.2—2.3 Å in *Psc*-**4b**, which are within the sum of van der Waals radii of an oxygen and a hydrogen atom and short enough to make the interaction possible.

We have been investigating differences in reactivity of rotational isomers by generating active chemical species such as 2-methyl-2-(substituted 9-triptycyl)propyl cation or radical rotamers. As a result, several interesting neighboring participations are recognized in the *sc*-forms, where the 1-substituent is located closely to the reaction center, by comparing with the results for the *ap*-forms, in which such interactions are not possible.[11,12] The X-ray structures should give important clues for understanding the differences in reactivity of rotational isomers, especially differences in the strengths of interactions between the 1-substituent and the reactive carbon center in *sc* compounds.

The nonbonding distances of C(20)–X for the amides should be regarded a model of distance between the reaction center and the 1-substituent, because the intermediates are often sp^2-hybridized whereas the model compounds here have the sp^3-hybridized carbons. The distances are in the range of 2.7—3.0 Å and obviously within the sum of van der Waals radii of the two atoms, X and C(20), this placement resulting in strong neighboring participations of the 1-substituent to the cation or radical center in the *sc* forms. The values increases in the order of *Psc*-**4b**(OCH_3)<*Psc*-**4c**(F)<*Psc*-**4d**(Cl)<*Psc*-**4a**(CH_3), and this order is generally in accordance with the steric size of the substituent except for the methoxy compound. This anomaly for the methoxy compound is possibly caused due to the attractive interactions discussed above.

In order to take the size of the substituent into account, we compare the values obtained by subtracting the effective radius[21] of 1-substituent from nonbonding distances; they are 1.28, 1.29, 1.40, and 1.32 Å for *Psc*-**4a** through **4d**, respectively. The distances are almost the same for CH_3, OCH_3, and Cl compounds whereas the fluoro compound has a larger value by 0.1 Å than the others. This difference can be important in determining the extent of interactions of the 1-substituent toward the reaction center.

We have reported an experimental finding that fluorine atoms undoubtedly stabilizes the neighboring cation but their stabilizing ability is much weaker than chlorines, from the product analysis of diazotization of *sc*-2-methyl-2-(1,2,3,4-tetrachloro- and tetrafluoro-9-triptycyl)propylamines.[22,23] Although this result, the poor stabilizing ability of the fluorine atom, will be mainly attributed to a larger ionization potential of its unshared electrons, which should participate in stabilizing the cation by electron transfer, than that of a chlorine atom, the distance between the two atoms may also be important in facilitating the interaction: The longer the distance, the much weaker the interaction. The contributions of the two factors to the stabilization cannot be separated from available data.

Experimental

Melting points are uncorrected. ^{1}H NMR spectra were measured on a Varian Gemini 300 spectrometer operating at 300.1 MHz. Optical rotation was measured on a JASCO DIP-370 polarimeter with the use of a 3.5 mmϕ×100 mm cell. CD spectra were measured with a JASCO J-600 spectropolarimeter at 23 °C as methanol solutions with concentration of ca. 1×10^{-3} mol L^{-1}, and a 0.2 mm cell was used for the measurement of the 200—280 nm region and a 2 mm one for 280—350 nm. UV spectra were recorded with a Hitachi U-2000 spectrophotometer for hexane solutions with concentration of ca. 1×10^{-3} mol L^{-1} or 5×10^{-5} mol L^{-1}. Elemental analyses were performed by a Perkin–Elmer 240C analyzer. Preparative HPLC was carried out with a Hitachi L-6250 pump using a Chemcosolb Si column (5 μm, 10 mmϕ×300 mm). Silica gel 60 F_{254} (Merck, 2 mm) was used for the preparative TLC. The racemic carboxylic acids were prepared according to the known method.[13,14] (1*S*,5*R*,7*R*)-10,10-Dimethyl-3-thia-4-azatricyclo[5.2.1.0^{1,5}]-decane 3,3-dioxide [(−)-10,2-camphorsultam] was synthesized according to the literature.[15]

The experimental procedure of the tetrachloro compounds is described in detail as a typical example. Optical resolution and syntheses were similarly carried out for the other compounds.

(1*S*,5*R*,7*R*)-10,10-Dimethyl-4-[3-methyl-*sc*-3-(1,2,-3,4-tetrachloro-9-triptycyl)butanoyl]-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decane 3,3-Dioxides (*Psc*-4d and *Msc*-4d). To a suspension of 10.8 mg (0.451 mmol) of sodium hydride (60% oil suspension) in 5 mL of dry benzene was added 90.6 mg (0.421 mmol) of (−)-10,2-camphorsultam. The solution was stirred for 30 min at room temperature. A benzene solution (5 mL) of ±*sc*-3-methyl-3-(1,2,-3,4-tetrachloro-9-triptycyl)butanoyl chloride, prepared from 211.5 mg (0.430 mmol) of the corresponding acid and 0.38 mL (4.3 mmol) of oxalyl dichloride in an ordinary manner, was transferred to the lithium amide solution. The mixture was stirred for 30 min at room temperature and then decomposed with 10 mL of water. The benzene layer was separated, dried over magnesium sulfate, and evaporated to afford a 1 : 1 mixture of diastereomers in an almost quantitative yield. The mixture was separated by HPLC with dichloromethane eluent and subsequent recrystallization from hexane–dichloromethane gave 135 mg of the first elution and 130 mg of the second elution, the combined yield being 89%. Each diastereomer was more than 99% pure according to the ^{1}H NMR spectra. A crystal of the first elution was submitted to the X-ray analysis and the absolute conformation was *Psc* about the C(9)–C(17) bond.

***Psc*-4d:** Mp 275.5—278.0 °C. Found: C, 60.80; H, 4.76; N, 1.99%. Calcd for $C_{35}H_{33}Cl_4NO_3S$: C, 60.97; H, 4.82; N, 2.03%. $[\alpha]_D^{23}-35°$ (*c* 0.38, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ=1.00 (3H, s), 1.31 (3H, s), 1.35—1.49 (2H, m), 1.84—2.00 (3H, m), 2.12 (3H, s), 2.14—2.34 (2H, m), 2.53 (3H, s), 3.46 and 3.52 (2H, ABq, J=13.7 Hz), 4.02 (1H, dd, J=5.1 and 7.5 Hz), 4.43 and 4.56 (2H, ABq, J=17.2 Hz), 6.08 (1H, s), 7.01—7.10 (4H, m), 7.39—7.48 (2H, m), 7.88 (1H, m), 7.98 (1H, m).

***Msc*-4d:** Mp 259.0—261.0 °C. Found: C, 56.01; H, 4.47; N, 1.89%. Calcd for $C_{35}H_{33}Cl_4NO_3S\cdot1/2CH_2Cl_2$: C, 55.83; H, 4.56; N, 1.81%. Recrystallization from dichloromethane gave crystals containing half a mole of solvent molecules. $[\alpha]_D^{23}-48°$ (*c* 0.39, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ=0.99 (3H, s), 1.24 (3H, s), 1.35—1.52 (2H, m), 1.83—2.02 (3H, m), 2.10—2.2 (2H, m), 2.22 (3H, s), 2.42 (3H, s), 3.45 and 3.50 (2H, ABq, J=13.6 Hz), 4.02 (1H, t, J=6.0 Hz), 4.25 and 4.51 (2H, ABq, J=18.7 Hz), 6.08 (1H, s), 7.01—7.13 (4H, m), 7.40—7.48 (2H, m), 7.91 (1H, m), 8.04 (1H, m).

Methyl [3(9′)-*Psc*]-3-Methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)butanoate (*Psc*-2d). To a suspension of 11.1 mg (0.292 mmol) of lithium aluminium hydride in 5 mL of dry tetrahydrofuran was added 101 mg (0.146 mmol) of the sultam amide (*Psc*-**4d**) under an argon atmosphere at room temperature. After the mixture was stirred for 30 min at the temperature, the solution was quenched with 10 mL of wet ether. The organic layer was decanted and washed with 10 mL of 5% aqueous sodium hydroxide for three times to remove the free camphorsultam and then with aqueous sodium chloride. After drying the solution over magnesium sulfate, the solvent was evaporated under a reduced pressure. The residue was purified by a preparative TLC and HPLC (eluent dichloromethane) to give 57 mg (81%) of the optically active alcohol.

[3(9′)-*Psc*]-3-Methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)-1-butanol (*Psc*-5d) showed the following physical and spectroscopic properties: Mp 153.0—156.0 °C; $[\alpha]_D^{23}+15°$ (*c* 0.90, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.48 (1H, br), 2.10 (3H, s), 2.13 (3H, s), 2.95 (1H, ddd, J=14.3, 9.0, and 5.7 Hz), 3.15 (1H, ddd, J=14.3, 9.3, and 6.0 Hz), 4.12—4.32 (2H, br m), 6.08 (1H, s), 7.01—7.11 (4H, m), 7.40—7.48 (2H, m), 7.92 (1H, m), 8.07 (1H, m).

To a solution of 57.0 mg (0.119 mmol) of the alcohol in 5 mL of acetone was added 0.10 mL of Jones reagent, prepared from 2.7 g of chromium(VI) oxide, 2.3 mL of sulfuric acid, and 7.0 mL of water, at room temperature. The reaction mixture was stirred for 1 h and color of the mixture gradually turned from orange to green during the course of the reaction. The mixture was quenched with 10 mL of water and extracted with 10 mL of dichloromethane for three times. The combined organic layer was washed with aqueous sodium chloride and dried over magnesium sulfate. Evaporation of the solution gave the carboxylic acid in 90% yield as white solid, which was used for the next reaction without purification.

[3(9′)-*Psc*]-3-Methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)butanoic Acid (*Psc*-3d) showed the following physical and spectroscopic properties: Mp 296—303 °C (with decomp); $[\alpha]_D^{25}+27°$ (*c* 0.49, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.25 (3H, s), 2.47 (3H, s), 3.86 and 4.23 (2H, ABq, J=15.4 Hz), 6.10 (1H, s), 7.03—7.16 (4H, m), 7.42—7.50 (2H, m), 7.93 (1H, m), 8.03 (1H, m). A signal due to the carboxyl proton could not be observed.

To a solution of 38.9 mg (0.079 mmol) of the carboxylic acid in 5 mL of ether was added an ethereal solution of a small excess of diazomethane at 0 °C. The solution was stirred for 1 h at the temperature and evaporated. The residue was purified by a preparative TLC (1 : 1 hexane–dichloromethane eluent) and the desired fraction was recrystallized from methanol. Yield was 86%. Mp 114.0—117.0 °C. Found: C, 61.93; H, 4.06%. Calcd for $C_{25}H_{20}O_2Cl_4$: C, 61.69; H, 3.98%. $[\alpha]_D^{25}+24°$ (*c* 0.66, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.15 (3H, s), 2.40 (3H, s), 3.76 and 4.14 (2H, ABq, J=15.2 Hz), 3.84 (3H, s), 6.08 (1H, s), 7.03—7.12

(4H, m), 7.41—7.49 (2H, m), 7.92 (1H, m), 8.05 (1H, m); UV (methanol, log ε in parentheses) 213.4 (4.76), 235 (4.47, sh), 262 (3.74, sh), 277 (3.38, sh), 292.6 (2.86), 301.6 nm (2.83). CD (methanol, $\Delta\varepsilon$ in parentheses) 201.0 (+12.1), 211.0 (−9.2), 218.5 (+12.0), 243.0 (−8.7), 263 (+4.2, sh), 267.5 (+4.4), 275 (+3.7, sh), 302.5 nm (+0.3). The optical purity was checked by ^{1}H NMR spectra in chloroform-*d* in the presence of ca. 0.3 equivalent of a chiral shift reagent, tris-[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]-europium(III) (Aldrich Chemical Co.). The racemic methyl ester gave two sets of signals with the same intensities; the methyl signal at δ=2.15 was split into two singlets with low field shift, for example. The resolved compound gave only one set and its optical purity was estimated to be better than 99%. The methyl signal at the higher field in the spectrum of the racemic material corresponds to the *Psc* compound.

Methyl [3(9′)-*Msc*]-3-Methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)butanoate (*Msc*-2d). This compound was similarly prepared from *Msc*-**4d** as described for the preparation of *Psc*-**2d**. Mp 113.5—117.0 °C. Found: C, 62.01; H, 4.05%. Calcd for $C_{25}H_{20}O_2Cl_4$: C, 61.69; H, 3.98%. $[\alpha]_D^{25}$ −23° (*c* 0.68, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ= 2.15 (3H, s), 2.40 (3H, s), 3.76 and 4.14 (2H, ABq, J=15.2 Hz), 3.84 (3H, s), 6.08 (1H, s), 7.03—7.13 (4H, m), 7.42—7.49 (2H, m), 7.92 (1H, m), 8.05 (1H, m).

The following physical and spectroscopic properties were recorded for the intermediates.

[3(9′)-*Msc*]-3-Methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)-1-butanol (*Msc*-5d). Mp 152.0—154.5 °C. $[\alpha]_D^{25}$ −16° (*c* 0.50, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.49 (1H, br), 2.10 (3H, s), 2.13 (3H, s), 2.95 (1H, ddd, J=14.3, 9.0, and 5.7 Hz), 3.15 (1H, ddd, J=14.3, 9.3, and 6.0 Hz), 4.12—4.31 (2H, m), 6.08 (1H, s), 7.01—7.11 (4H, m), 7.40—7.48 (2H, m), 7.92 (1H, m), 8.08 (1H, m).

[3(9′)-*Msc*]-3-Methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)butanoic Acid (*Msc*-3d): Mp 301—307 °C (with decomp), $[\alpha]_D^{25}$ −26° (*c* 0.32, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.25 (3H, s), 2.47 (3H, s), 3.86 and 4.23 (2H, ABq, J=15.4 Hz), 6.10 (1H, s), 7.04—7.16 (4H, m), 7.42—7.51 (2H, m), 7.93 (1H, m), 8.03 (1H, m).

(1*S*,5*R*,7*R*)-10,10-Dimethyl-4-[*sc*-3-(1,4-dimethyl-9-triptycyl)-3-methylbutanoyl]-3-thia-4-azatricyclo-[5.2.1.0^{1,5}]decane 3,3-Dioxides (*Psc*-4a and *Msc*-4a). A mixture of diastereomers was similarly prepared from ±*sc*-3-(1,4-dimethyl-9-triptycyl)-3-methylbutanoic acid as described in the preparation of *Psc*-**4d** and *Msc*-**4d**. The crude material was chromatographed on silica gel with 2:3 hexane–dichloromethane eluent. The diastereomers were separated by HPLC with 2:1 hexane–ether eluent. The combined yield was 83%. The first elution was found to be the *Psc* from its X-ray analysis.

***Psc*-4a:** Mp 302.0—303.0 °C. Found: C, 76.72; H, 7.09; N, 2.60%. Calcd for $C_{37}H_{41}NO_3S$: C, 76.65; H, 7.13; N, 2.42%. $[\alpha]_D^{25}$ −53° (*c* 0.84, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=0.99 (3H, s), 1.30 (3H, s), 1.30—1.52 (2H, m), 1.81—1.98 (3H, m), 2.17 (3H, m), 2.14—2.32 (2H, m), 2.44 (3H, s), 2.52 (3H, s), 2.77 (3H, s), 3.44 and 3.51 (2H, ABq, J=13.7 Hz), 3.91 and 4.45 (2H, ABq, J=17.1 Hz), 4.01 (1H, dd, J=7.4 and 5.2 Hz), 5.57 (1H, s), 6.78 (2H, s), 6.93—7.02 (4H, m), 7.30—7.38 (2H, m), 7.83 (1H, m), 8.01 (1H, m).

***Msc*-4a:** Mp 269.0—270.0 °C. Found: C, 76.96; H, 7.19; N, 2.42%. Calcd for $C_{37}H_{41}NO_3S$: C, 76.65; H, 7.13; N, 2.42%. $[\alpha]_D^{25}$ −67° (*c* 0.83, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=0.98 (3H, s), 1.21 (3H, s), 1.34—1.49 (2H, m), 1.88—1.97 (3H, m), 2.15—2.25 (2H, m), 2.28 (3H, s), 2.32 (3H, s), 2.52 (3H, s), 2.62 (3H, s), 3.42 and 3.47 (2H, ABq, J=13.7 Hz), 4.01 (1H, t, J=6.3 Hz), 4.18 and 4.29 (2H, ABq, J=19.0 Hz), 5.57 (1H, s), 6.76 and 6.77 (2H, ABq, J=8.3 Hz), 6.93—7.02 (4H, m), 7.30—7.38 (2H, m), 7.83 (1H, m), 7.89 (1H, m).

Methyl [3(9′)-*Psc*]-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoate (*Psc*-2a). This compound was similarly prepared from *Psc*-**4a** as described for the preparation of *Psc*-**2d**. Overall yield was 52%. Mp 210.0—211.5 °C. Found: C, 84.71; H, 7.04%. Calcd for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12%. $[\alpha]_D^{25}$ +32° (*c* 0.80, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.22 (3H, s), 2.30 (3H, s), 2.52 (3H, s), 2.71 (3H, s), 3.67 and 3.84 (2H, ABq, J=15.9 Hz), 3.84 (3H, s), 5.58 (1H, s), 6.78 (2H, s), 6.95—7.02 (4H, m), 7.31—7.40 (2H, m), 7.84 (1H, m), 7.93 (1H, m); CD (methanol, $\Delta\varepsilon$ in parentheses) 211.0 (−5.3), 217.0 (+1.0), 225.0 (−4.7), 249.0 (−4.4), 270.0 (+1.5), 277.0 (+1.5), 291.0 (−0.1). UV data were reported in the literature.[6]

The following physical and spectroscopic properties were recorded for the intermediates.

[3(9′)-*Psc*]-3-(1,4-Dimethyl-9-triptycyl)-3-methyl-1-butanol (*Psc*-5a): Mp 127—133 °C (with decomp); $[\alpha]_D^{25}$ +17° (*c* 0.83, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.06 (3H, s), 2.13 (3H, s), 2.52 (3H, s), 2.65 (3H, s), 2.90 (1H, ddd, J=14.7, 9.2, and 6.0 Hz), 3.01 (1H, ddd, J=14.7, 8.9, and 5.8 Hz), 4.17—4.29 (2H, m), 5.58 (1H, s), 6.77 (2H, s), 6.92—7.01 (4H, m), 7.31—7.39 (2H, m), 7.83 (1H, m), 7.98 (1H, m).

[3(9′)-*Psc*]-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoic Acid (*Psc*-3a): Mp 144—155 °C (with decomp); $[\alpha]_D^{25}$ +27° (*c* 0.84, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ= 2.30 (3H, s), 2.37 (3H, s), 2.52 (3H, s), 2.75 (3H, s), 3.76 and 3.93 (2H, ABq, J=15.9 Hz), 5.60 (1H, s), 6.80 (2H, s), 6.95—7.08 (4H, m), 7.33—7.41 (2H, m), 7.86 (1H, m), 7.93 (1H, m).

Methyl [3(9′)-*Msc*]-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoate (*Msc*-2a). This compound was prepared from *Msc*-**4a** as described for the preparation of *Psc*-**2d**. Mp 210.0—211.5 °C. Found: C, 84.63; H, 7.03%. Calcd for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12%. $[\alpha]_D^{25}$ −32° (*c* 0.80, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.23 (3H, s), 2.30 (3H, s), 2.52 (3H, s), 2.71 (3H, s), 3.67 and 3.84 (2H, ABq, J=15.8 Hz), 3.84 (3H, s), 5.58 (1H, s), 6.78 (2H, s), 6.96—7.02 (4H, m), 7.31—7.40 (2H, m), 7.84 (1H, m), 7.93 (1H, m).

The following physical and spectroscopic properties of the intermediates were recorded.

[3(9′)-*Msc*]-3-(1,4-Dimethyl-9-triptycyl)-3-methyl-1-butanol (*Msc*-5a): Mp 126—134 °C (with decomp); $[\alpha]_D^{25}$ −17° (*c* 0.83, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.04 (3H, s), 2.12 (3H, s), 2.52 (3H, s), 2.64 (3H, s), 2.90 (1H, ddd, J=14.7, 9.1, and 6.0 Hz), 3.00 (1H, ddd, J=14.7, 8.9, and 5.7 Hz), 4.13—4.28 (2H, m), 5.57 (1H, s), 6.76 (2H, s), 6.92—7.01 (4H, m), 7.31—7.39 (2H, m), 7.82 (1H, m), 7.97 (1H, m).

[3(9′)-*Msc*]-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoic Acid (*Msc*-3a): Mp 144—154 °C (with decomp); $[\alpha]_D^{25}$ −27° (*c* 0.82, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ= 2.30 (3H, s), 2.37 (3H, s), 2.53 (3H, s), 2.75 (3H, s), 3.76 and 3.93 (2H, ABq, J=15.9 Hz), 5.60 (1H, s), 6.80 (2H, s),

6.96—7.08 (4H, m), 7.32—7.41 (2H, m), 7.86 (1H, m), 7.93 (1H, m).

(1*S*,5*R*,7*R*)-4-[*sc*-3-(1,4-Dimethoxy-9-triptycyl)-3-methylbutanoyl]-10,10-dimethyl-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decane 3,3-Dioxides (*Psc*-4b and *Msc*-4b). A mixture of diastereomeric sultam amides was similarly prepared from racemic *sc*-3-(1,4-dimethoxy-9-triptycyl)-3-methylbutanoic acid as described for the preparation of *Psc*-**4d** and *Msc*-**4d**. Treatment of the mixture with dichloromethane predominantly afforded one diastereomer as crystals, which was recrystallized from chloroform to give crystals with one mole solvent of crystallization. The better soluble isomer was purified by HPLC (eluent: dichloromethane) and subsequent recrystallization from dichloromethane–hexane, and found to be a *Psc* form from the X-ray analysis. The combined yield was 86%.

***Psc*-4b:** Mp 274.0—275.0 °C. Found: C, 72.35; H, 6.67; N, 2.25%. Calcd for $C_{37}H_{41}NO_5S$: C, 72.64; H, 6.76; N, 2.29%. $[\alpha]_D^{25}-49°$ (*c* 0.97, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.00 (3H, s), 1.32 (3H, s), 1.34—1.50 (2H, m), 1.84—2.01 (3H, br m), 2.08—2.32 (2H, m), 2.12 (3H, s), 2.26 (3H, s), 3.41 and 3.49 (2H, ABq, J=13.7 Hz), 3.74 (3H, s), 3.82 (3H, s), 4.01 (1H, dd, J=4.9 and 7.1 Hz), 4.26 and 4.47 (2H, ABq, J=17.1 Hz), 5.87 (1H, s), 6.58 and 6.65 (2H, ABq, J=8.9 Hz), 6.91—7.02 (4H, m), 7.33—7.42 (2H, m), 7.77 (1H, m), 7.88 (1H, m).

***Msc*-4b:** Mp 243.0—245.0 °C. Found: C, 62.22; H, 5.83; N, 1.89%. Calcd for $C_{37}H_{41}NO_5S\cdot CHCl_3$: C, 62.42; H, 5.79; N, 1.92%. $[\alpha]_D^{25}-52°$ (*c* 0.87, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=0.99 (3H, s), 1.26 (3H, s), 1.34—1.50 (2H, m), 1.83—2.01 (3H, br m), 2.09—2.30 (2H, m), 2.17 (3H, s), 2.19 (3H, s), 3.43 and 3.48 (2H, ABq, J=13.7 Hz), 3.71 (3H, s), 3.82 (3H, s), 4.02 (1H, dd, J=4.9 and 7.1 Hz), 4.16 and 4.54 (2H, ABq, J=17.9 Hz), 5.88 (1H, s), 6.57 and 6.64 (2H, ABq, J=9.0 Hz), 6.91—7.05 (4H, m), 7.33—7.42 (2H, m), 7.79 (1H, m), 8.00 (1H, m).

Methyl [3(9′)-*Psc*]-3-(1,4-Dimethoxy-9-triptycyl)-3-methylbutanoate (*Psc*-2b). This compound was similarly prepared from *Psc*-**4b** as described for the preparation of *Psc*-**2d**. Overall yield was 58%. Mp 172.5—174.0 °C. Found: C, 78.16; H, 6.40%. Calcd for $C_{28}H_{28}O_4$: C, 78.48; H, 6.59%. $[\alpha]_D^{25}+20°$ (*c* 0.69, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.14 (3H, s), 2.15 (3H, s), 3.61 and 3.99 (2H, ABq, J=14.6 Hz), 3.75 (3H, s), 3.82 (3H, s), 3.83 (3H, s), 5.89 (1H, s), 6.59 and 6.64 (2H, ABq, J=8.9 Hz), 6.93—7.02 (4H, m), 7.37—7.42 (2H, m), 7.82 (1H, m), 7.92 (1H, m); CD (methanol, $\Delta\varepsilon$ in parentheses) 201.0 (+8.1), 207.0 (−0.3), 217.0 (+8.3), 237.0 (−1.5), 254.0 (+1.7), 278.5 (−0.7), 296.5 (+0.5), 300.0 (+0.3), 308.0 nm (+0.5). UV data were reported in the literature.[6)]

The following physical and spectroscopic properties were recorded for the intermediates.

[3(9′)-*Psc*]-3-(1,4-Dimethoxy-9-triptycyl)-3-methyl-1-butanol (*Psc*-5b): Mp 125.0—129.0 °C; $[\alpha]_D^{25}+8.2°$ (*c* 0.45, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.95 (3H, s), 2.08 (3H, s), 2.80 (1H, dt, J=14.1 and 7.8 Hz), 2.97 (1H, dt, J=14.1 and 7.8 Hz), 3.76 (3H, s), 3.82 (3H, s), 4.17 (1H, br m), 5.89 (1H, s), 6.60 and 6.64 (2H, ABq, J=9.0 Hz), 6.91—7.01 (4H, m), 7.35—7.41 (2H, m), 7.83 (1H, m), 7.94 (1H, m).

[3(9′)-*Psc*]-3-(1,4-Dimethoxy-9-triptycyl)-3-methylbutanoic Acid (*Psc*-3b): Mp 235—241 °C (with decomp); $[\alpha]_D^{25}+20°$ (*c* 0.94, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.22 (3H, s), 2.24 (3H, s), 3.69 and 4.09 (2H, ABq, J=14.9 Hz), 3.79 (3H, s), 3.83 (3H, s), 5.91 (1H, s), 6.56 and 6.61 (2H, ABq, J=9.0 Hz), 6.94—7.06 (4H, m), 7.36—7.47 (2H, m), 7.84 (1H, m), 7.93 (1H, m).

Methyl [3(9′)-*Msc*]-3-(1,4-Dimethoxy-9-triptycyl)-3-methylbutanoate (*Msc*-2b). This compound was prepared from *Msc*-**4b** similarly as described for the preparation of *Psc*-**2d**. Mp 173.0—174.5 °C. Found: C, 78.19; H, 6.39%. Calcd for $C_{28}H_{28}O_4$: C, 78.48; H, 6.59%. $[\alpha]_D^{25}-20°$ (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.14 (3H, s), 2.15 (3H, s), 3.61 and 3.98 (2H, ABq, J=14.6 Hz), 3.75 (3H, s), 3.82 (3H, s), 3.83 (3H, s), 5.89 (1H, s), 6.59 and 6.64 (2H, ABq, J=8.9 Hz), 6.92—7.02 (4H, m), 7.37—7.41 (2H, m), 7.82 (1H, m), 7.93 (1H, m).

The following physical and spectroscopic properties of the intermediates were recorded.

[3(9′)-*Msc*]-3-(1,4-Dimethoxy-9-triptycyl)-3-methyl-1-butanol (*Msc*-5b): Mp 136.0—139.0 °C; $[\alpha]_D^{25}-8.8°$ (*c* 0.41, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.96 (3H, s), 2.08 (3H, s), 2.80 (1H, dt, J=14.2 and 7.7 Hz), 2.97 (1H, dt, J=14.2 and 7.7 Hz), 3.77 (3H, s), 3.82 (3H, s), 4.17 (2H, br t, J=7.7 Hz), 5.89 (1H, s), 6.61 and 6.63 (2H, ABq, J=8.9 Hz), 6.92—7.02 (4H, m), 7.35—7.42 (2H, m), 7.83 (1H, m), 7.94 (1H, m).

[3(9′)-*Msc*]-3-(1,4-Dimethoxy-9-triptycyl)-3-methylbutanoic Acid (*Msc*-3b): Mp 234—238 °C (with decomp); $[\alpha]_D^{25}-21°$ (*c* 0.91, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.22 (3H, s), 2.24 (3H, s), 3.70 and 4.09 (2H, ABq, J=15.1 Hz), 3.79 (3H, s), 3.83 (3H, s), 5.91 (1H, s), 6.61 and 6.66 (2H, ABq, J=9.0 Hz), 6.94—7.06 (4H, m), 7.36—7.46 (2H, m), 7.84 (1H, m), 7.93 (1H, m).

(1*S*,5*R*,7*R*)-10,10-Dimethyl-4-[3-methyl-*sc*-3-(1,2,-3,4-tetrafluoro-9-triptycyl)butanoyl]-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decane 3,3-Dioxides (*Psc*-4c and *Msc*-4c). A mixture of diastereomers was prepared from racemic *sc*-3-methyl-3-(1,2,3,4-tetrafluoro-9-triptycyl)-butanoic acid as described for the preparation of *Psc*-**4d** and *Msc*-**4d**. The crude material was chromatographed on silica gel with 2:3 hexane–dichloromethane eluent. The diastereomers were completely separated by one recrystallization from hexane–dichloromethane. The less soluble diastereomer was submitted to X-ray analysis and its absolute conformation was *Psc*.

***Psc*-4c:** Mp 291.0—292.0 °C (with decomp). Found: C, 67.14; H, 5.22; N, 2.27%. Calcd for $C_{35}H_{33}NF_4O_3S$: C, 67.40; H, 5.33; N, 2.25%. $[\alpha]_D^{25}-70°$ (*c* 0.80, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.02 (3H, s), 1.32 (3H, s), 1.35—1.52 (2H, m), 1.86—2.02 (3H, m), 2.14 (3H, s), 2.15—2.32 (2H, m), 2.26 (3H, d, J=8.9 Hz), 3.63 and 3.68 (2H, ABq, J=13.8 Hz), 3.66 (1H, dd, J=17.0 and 7.1 Hz), 4.03 (1H, dd, J=7.6 and 5.1 Hz), 4.26 (1H, d, J=17.0 Hz), 5.67 (1H, s), 7.00—7.09 (4H, m), 7.38—7.43 (2H, m), 7.76 (1H, m), 7.89 (1H, m).

***Msc*-4c:** Mp 191.0—194.0 °C. Found: C, 67.51; H, 5.23; N, 2.47%. Calcd for $C_{35}H_{33}NF_4O_3S$: C, 67.40; H, 5.33; N, 2.25%. $[\alpha]_D^{25}-44°$ (*c* 0.78, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=0.99 (3H, s), 1.25 (3H, s), 1.34—1.52 (2H, m), 1.90—1.99 (3H, m), 2.13 (3H, d, J=9.6 Hz), 2.15—2.28 (2H, m), 2.25 (3H, s), 3.37 and 3.49 (2H, ABq, J=13.8 Hz), 3.74 (1H, d, J=18.1 Hz), 4.02 (1H, dd, J=7.9 and 5.0 Hz), 4.08 (1H, dd, J=18.1 and 3.1 Hz), 5.67 (1H, s), 7.00—7.09 (4H, m), 7.38—7.43 (2H, m), 7.78 (1H, m), 7.91 (1H, m).

Table 6. Crystal and Structure Analysis Data of Compounds *Psc*-**4a**—**d**

Compound	*Psc*-**4a**	*Psc*-**4b**	*Psc*-**4c**	*Psc*-**4d**
Formula	$C_{37}H_{41}NO_3S$	$C_{37}H_{41}NO_5S$	$C_{35}H_{33}F_4NO_3S$	$C_{35}H_{33}Cl_4NO_3S$
F.W.	579.80	611.80	623.71	689.53
Crystal size/mm^3	0.40×0.30×0.20	0.35×0.30×0.30	0.45×0.30×0.30	0.30×0.30×0.25
Scan rate/°min^{-1}	4	4	4	3
Scan range A/° a)	1.01	0.97	0.93	0.92
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P1$
a/Å	16.529(6)	10.846(2)	10.548(2)	10.155(2)
b/Å	18.346(6)	10.858(2)	28.611(6)	10.627(2)
c/Å	10.316(4)	27.577(7)	9.970(2)	8.875(2)
α/°	90	90	90	109.17(2)
β/°	90	90	90	108.94(1)
γ/°	90	90	90	61.60(2)
V/Å^3	3128(2)	3248(2)	3009(1)	779.3(7)
Z	4	4	4	1
D_c/g cm^{-3}	1.23	1.25	1.38	1.47
μ/cm^{-1}	1.03	1.05	1.27	4.85
2θrange/°	2—61	2—60	2—60	2—60
No. of data	4510	5282	4361	4432
No. of data used b)	3551	3860	3600	3555
B b)	2	3	2	3
g	0	1.3×10^{-5}	3.2×10^{-5}	—
R	0.053	0.064	0.059	0.034
R_w	0.041	0.060	0.054	0.020

a) Scan range was calculated by $A°+0.35°\tan\theta$. b) Reflections within $|F_o|>B\sigma(F_o)$ were used for structural refinement.

Methyl [3(9′)-*Psc*]-3-Methyl-3-(1,2,3,4-tetrafluoro-9-triptycyl)butanoate (*Psc*-2c). This compound was similarly prepared from *Psc*-**4c** as described for the preparation of *Psc*-**2d** and overall yield was 52%. The pure material was obtained by recrystallization from ethanol. Mp 86.0—88.5 °C. Found: C, 71.15; H, 4.55%. Calcd for $C_{26}H_{20}O_2F_4$: C, 70.90; H, 4.58%. $[\alpha]_D^{25}-2.2°$ (c 0.83, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.13 (3H, d, J=8.1 Hz), 2.16 (3H, s), 3.37 and 3.61 (2H, ABq, J=14.8 Hz), 3.84 (3H, s), 5.69 (1H, br s), 7.00—7.11 (4H, m), 7.39—7.46 (2H, m), 7.81 (1H, m), 7.94 (1H, m); UV (methanol, log ε in parentheses) 212.8 (4.59), 255.8 (3.18), 269.0 (3.18), 276.8 nm (3.15). CD (methanol, $\Delta\varepsilon$ in parentheses) 208.5 (−5.3), 217.0 (+4.4), 229 (−1.5, sh), 233.0 (−2.2), 249.0 (+1.3), 265.5 (−0.2), 267.5 (+0.3), 269.5 (−0.03), 271.5 (+0.4), 274.5 (−0.03), 277.0 nm (+0.47).

The following physical and spectroscopic properties of the intermediates were recorded.

[3(9′)-*Psc*]-3-Methyl-3-(1,2,3,4-tetrafluoro-9-triptycyl)-1-butanol (*Psc*-5c): Mp 124.5—128.0 °C; $[\alpha]_D^{25}$ −6.2° (c 0.78, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.92 (3H, d, J=7.2 Hz), 2.12 (3H, s), 2.44—2.57 (1H, m), 2.76—2.89 (1H, m), 4.12—4.28 (2H, m), 5.69 (1H, d, J=1.2 Hz), 7.01—7.09 (4H, m), 7.39—7.47 (2H, m), 7.85 (1H, m), 7.95 (1H, m).

[3(9′)-*Psc*]-3-Methyl-3-(1,2,3,4-tetrafluoro-9-triptycyl)butanoic Acid (*Psc*-3c): Mp 295—297 °C (with decomp); $[\alpha]_D^{25}-0.7°$ (c 0.88, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.20 (3H, d, J=8.1 Hz), 2.25 (3H, s), 3.46 (1H, dd, J=15.3 and 1.8 Hz), 3.70 (1H, d, J=15.3 Hz), 5.72 (1H, br s), 7.05—7.16 (4H, m), 7.40—7.49 (2H, m), 7.84 (1H, m), 7.93 (1H, m).

Methyl [3(9′)-*Msc*]-3-Methyl-3-(1,2,3,4-tetrafluoro-9-triptycyl)butanoate (*Msc*-2c). This compound was prepared from *Msc*-**4c** similarly as described for the preparation of *Psc*-**2d**. Mp 87.5—88.5 °C. Found: C, 71.01; H, 4.59%. Calcd for $C_{26}H_{20}O_2F_4$: C, 70.90; H, 4.58%. $[\alpha]_D^{25}+2.2°$ (c 0.80, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ=2.14 (3H, d, J=8.1 Hz), 2.16 (3H, s), 3.37 and 3.61 (2H, ABq, J=14.8 Hz), 3.84 (3H, s), 5.69 (1H, br s), 7.00—7.11 (4H, m), 7.39—7.46 (2H, m), 7.82 (1H, m), 7.94 (1H, m).

The following physical and spectroscopic properties were recorded for the intermediates.

[3(9′)-*Msc*]-3-Methyl-3-(1,2,3,4-tetrafluoro-9-triptycyl)-1-butanol (*Msc*-5c): Mp 124.5—128.0 °C; $[\alpha]_D^{25}+5.1°$ (c 0.85, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.92 (3H, d, J=7.2 Hz), 2.12 (3H, s), 2.44—2.58 (1H, m), 2.78—2.89 (1H, m), 4.13—4.28 (2H, m), 5.68 (1H, d, J=1.2 Hz), 7.00—7.09 (4H, m), 7.39—7.47 (2H, m), 7.84 (1H, m), 7.95 (1H, m).

[3(9′)-*Msc*]-3-Methyl-3-(1,2,3,4-tetrafluoro-9-triptycyl)butanoic Acid (*Msc*-3c): Mp 294—296 °C (with decomp); $[\alpha]_D^{25}+1.1°$ (c 0.72, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.21 (3H, d, J=8.1 Hz), 2.26 (3H, s), 3.47 (1H, dd, J=15.3 and 1.8 Hz), 3.71 (1H, d, J=15.3 Hz), 5.72 (1H, br s), 7.05—7.15 (4H, m), 7.41—7.49 (2H, m), 7.84 (1H, m), 7.93 (1H, m).

X-Ray Crystallography.[24] Crystals used for the X-ray diffraction were grown from hexane–dichloromethane solutions for compounds *Psc*-**4b**—**4d** and from a hexane–tetrahydrofuran solution for compound *Psc*-**4a**. X-Ray data were collected on a MAC Science MXC18 four circle diffractometer with Mo $K\alpha$ radiation (λ=0.71073 Å). The scan

mode was the 2θ method in the range of $2\theta<30°$ and the ω–2θ method in $2\theta>30°$. The scan range was calculated by $A°+0.35°\tan\theta$, where the value of A is given in Table 6. The structures were solved by the direct method and refined by the full-matrix least-squares method by using the CRYSTAN program for compounds *Psc*-**4a**—**4c** and the TEXSAN program for *Psc*-**4d**. Anisotropic and isotropic thermal parameters were employed for non-hydrogen and hydrogen atoms, respectively. No absorption correction was applied. Reflections within $|F_o|>B\sigma(F_o)$, where B's are given in Table 6, were used for the structure determination and refinement. The function minimized was $\sum[w(|F_o|^2-|F_c|^2)^2]$, where $w=[(\sigma_c|F_o|)^2+g|F_o|^2]^{-1}$, in the CRYSTAN program, and $\sum[w(|F_o|-|F_c|)^2]$, where $w=(\sigma_c^2|F_o|)^{-1}$, in the TEXSAN program. For the calculation of compound *Psc*-**4d**, the Cl(1) atom was fixed at the same position during the refinement. Additional crystal and analysis data are listed in Table 6.

The authors thank Professor K. Takeda and Dr. Y. Moriyama of this University for measuring the CD spectra. The X-ray analyses were performed at the Analytical Center of the University. The authors wish to express their thanks to Dr. H. Akashi of the Center for his assistance in X-ray analysis. We are also indebted to Professor N. Harada of Tohoku University for his kind suggestion of using the camphorsultam for resolution.

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24) Tables of coordinates for the hydrogen atoms, anisotropic thermal parameters of the non-hydrogen atoms, and complete F_o-F_c data are deposited as Document No. 67038 at the Office of the Editor of Bull. Chem. Soc. Jpn.