$\omega/2\theta$ scans	$\theta_{max} = 74.26°$
Absorption correction: empirical *via* ψ scan data (Fair, 1990)	$h = -7 \rightarrow 0$
	$k = -9 \rightarrow 0$
	$l = -25 \rightarrow 0$
$T_{min} = 0.941$, $T_{max} = 0.999$	3 standard reflections
1068 measured reflections	every 250 reflections
1068 independent reflections	intensity decay: 2.7%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.192$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.031$	$\Delta\rho_{min} = -0.139$ e Å^{-3}
$wR(F^2) = 0.090$	Extinction correction: *SHELXL*93
$S = 1.132$	Extinction coefficient: 0.0160 (14)
1068 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
129 parameters	
H atoms calculated and refined as riding atoms with $U = 1.2$(or 1.5)U_{host}	Absolute structure: Flack (1983)
	Flack parameter = −0.2 (4)
$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.1854P]$ where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{max} < 0.001$	

Table 1. *Selected geometric parameters (Å, °)*

C1—O7	1.386 (2)	C8—C9	1.539 (3)
C1—C6	1.397 (3)	O8—C10	1.420 (3)
C6—C10	1.490 (3)	C9—O9	1.191 (3)
O7—C8	1.438 (2)	C9—O10	1.347 (3)
C8—O8	1.407 (3)	O10—C10	1.454 (3)
C1—O7—C8	115.59 (15)	C9—O10—C10	105.8 (2)
C8—O8—C10	101.8 (2)		

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *DIAMOND* (Brandenburg, 1996). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1270). Services for accessing these data are described at the back of the journal.

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sp-(*R*)-9-(*o*-*tert*-Butylphenyl)-9-hydroxy-*N*-[(*S*)-α-methylbenzyl]fluorene-2-carboxamide–Acetone: a Novel 1:1 Cavitate

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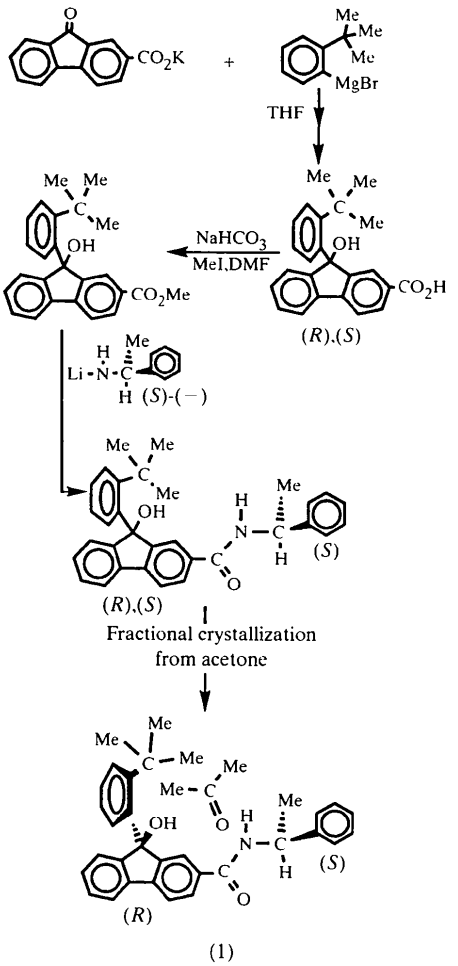
Abstract

Fractional crystallization of the two epimers *sp*-(*R*),(*S*)-9-(*o*-*tert*-butylphenyl)-9-hydroxy-*N*-[(*S*)-1-phenylethyl]-fluorene-2-carboxamide from acetone provided the title epimer as a 1:1 cavitate ($C_{32}H_{31}NO_2.C_3H_6O$) with the solvent acetone. Hydrogen bonding between the NH group of the host molecule and the O atom of a molecule of acetone takes place within a cavity of the host molecule, forming the novel cavitate. In addition, molecules of the host are connected to one another through hydrogen bonds between their respective OH groups as donors and amide O atoms as acceptors, forming molecular chains. To accommodate the molecule of acetone and its hydrogen bonding within the cavity, the *o*-*tert*-butylphenyl group of the title host, in contrast to that in its parent *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenol, is substantially rotated away from perpendicularity with the fluorene plane.

Comment

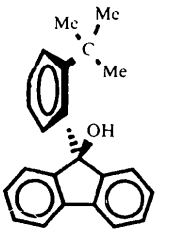
During the course of our investigations of the stereochemistry associated with reactions of sterically-hindered rotationally-restricted 9-arylfluorenes, it was necessary to prepare several enantiomerically pure 2-methyl-9-(*o*-*tert*-butylphenyl)fluorene compounds. This was accomplished subsequent to a multistep synthesis of the two epimeric *sp*-(*R*),(*S*)-9-(*o*-*tert*-butylphenyl)-9-hydroxy-*N*-[(*S*)-α-methylbenzyl]fluorene-2-carboxamide, starting from commercially available 9-fluorenone-2-carboxylic acid and (*S*)-(−)-α-methylbenzylamine (see scheme below) (Hou, 1997). Of the two epimers, one was more readily isolated by fractional crystallization of the mixture from methanol, ethanol or acetone. ^{1}H NMR ($CDCl_3$) analysis of the crystals isolated from these solvents consistently exhibited the presence of a mole equivalent of the respective solvent. While the methanol and ethanol solvents evaporated from the crystals after a day or two, leaving an amorphous solid, the crystals obtained from acetone retained their transparency, and NMR indicated that acetone was still

present in equimolar amounts with the epimer after several weeks. Crystallization from non-hydrogen-bonding solvents (*e.g.* hexanes, methylene chloride) always produced very fine needle clusters unsuitable for X-ray diffraction. Moreover, the other epimer did not appear to crystallize well from either of the two alcohols or acetone. These results suggested that each molecule of the easily crystallized epimer formed an inclusion-type compound through hydrogen bonding with a molecule of solvent, and that there may be functional and geometric requirements for the solvent molecule to effect a stable crystalline form of the epimer. An X-ray diffraction study was undertaken.



(1)

The X-ray structure of the epimer with co-crystallized acetone, and the atom labeling, are shown in Fig. 1. The epimer, *sp*-(*R*)-9-(*o*-*tert*-butylphenyl)-9-hydroxy-*N*-[(*S*)-α-methylbenzyl]fluorene-2-carboxamide, is clearly the host in a crystalline cavitate, (1) (see Eliel & Wilen, 1994), a single molecule of acetone neatly residing in the cavity of the conformation adopted by each host molecule to maintain a hydrogen bond, N1—H1*a*···O3, between the amide NH group of the host and the O atom of the acetone. In addition, the molecules of the host are connected to one another through hydrogen bonds, O1—H1*b*···O2($1-x$, $y-\frac{1}{2}$, $-z$), between their respective OH groups as donors and amide O atoms as acceptors, forming molecular chains (Fig. 2). The influence of the molecule of acetone on the structure of the host is best appreciated by comparison of the structure of the host with that of its parent non-cavitate compound, *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenol, (2) (Robinson *et al.*, 1998). While the 9-aryl and fluorenyl planes of



(2)

(2) are essentially perpendicular, the 9-aryl ring in (1) is rotated 13.74(17)° away from perpendicularity with the fluorene plane. The X-ray structure clearly shows that this rotation is effected by the methyl groups of the acetone molecule impinging on the 9-aryl ring, *viz* H19*b*···C3′, H19*b*···C4′, H21*c*···C5′ and H21*c*···C6′. As a result, the torsion angle C6′—C1′—C9—C9a is much larger than C6′—C1′—C9—C8a, and C2′—C1′—C9—O1 and C6′—C1′—C9—O1 deviate substantially from the near coplanarity shown by the corresponding torsion angles of (2). The geometric stability being easily accomplished through rotation, no bonding distortion is apparent and the other parameters of (1) are essentially the same as the corresponding parameters of (2).

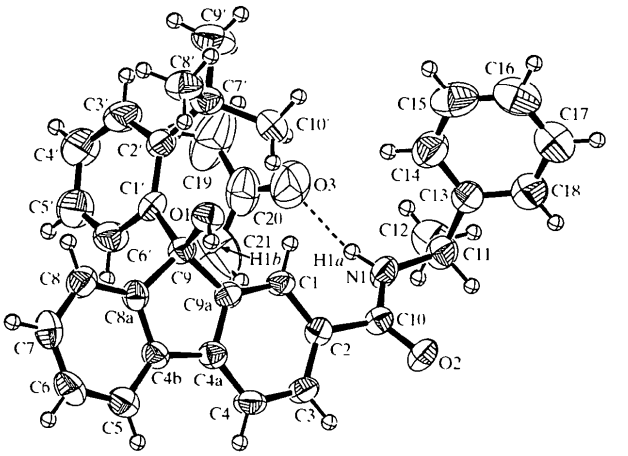


Fig. 1. The molecular structure and atom-numbering scheme for (1) with displacement ellipsoids at the 50% probability level.

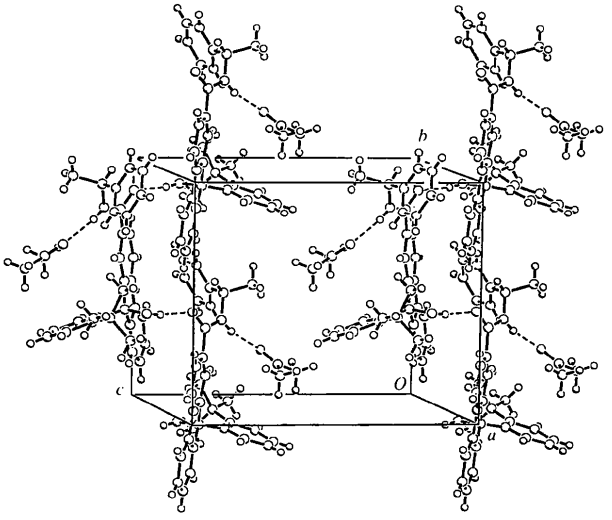


Fig. 2. The molecular packing and hydrogen bonding of (1). Molecular chains, a result of the hydrogen bonding, propagate parallel to [010].

The discovery that acetone, and possibly methanol and ethanol, selectively forms a cavitate with one of the two epimers makes this epimer a candidate as a host molecule for chiral recognition (Eliel & Wilen, 1994). ^{1}H NMR ($CDCl_3$) analysis of the title epimer recrystallized from *rac*-2-butanol indeed showed that the crystals contained a molar equivalent of one enantiomer of 2-butanol. However, an attempt to identify the absolute configuration of the enantiomer by X-ray structural analysis was unsuccessful because of unresolvable solvent disorder.

Experimental

The multistep synthesis of the epimer mixture from 9-fluorenone-2-carboxylic acid (Aldrich Chemical Co.) and (*S*)-(−)-α-methylbenzylamine (Acros Organics), and the isolation of (1) by recrystallization from acetone will be described elsewhere. ^{1}H NMR ($CDCl_3$) analysis of the dried white crystalline (1) (m.p. 467–468 K, corrected; brown melt) correctly identified it as a 1:1 host–guest compound.

Crystal data

$C_{32}H_{31}NO_2.C_3H_6O$
M_r = 519.68
Monoclinic
$P2_1$
a = 8.570 (2) Å
b = 12.4127 (15) Å
c = 14.549 (2) Å
β = 106.502 (15)°
V = 1484.0 (4) Å^3
Z = 2
D_x = 1.163 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 9.35–12.12°
μ = 0.073 mm^{-1}
T = 296 K
Prism
0.43 × 0.30 × 0.27 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans (3° min^{-1} in ω)
Absorption correction: none
3811 measured reflections
3580 independent reflections
1706 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 27.52°
h = 0 → 11
k = 0 → 16
l = −18 → 18
3 standard reflections
every 150 reflections
intensity decay: 0.20%

Refinement

Refinement on F^2
$R(F)$ = 0.038
$wR(F^2)$ = 0.092
S = 1.145
3579 reflections
356 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.151 e Å^{-3}
$\Delta\rho_{min}$ = −0.137 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: ascertained from the known configuration of the (*S*)-(−)-α-methylbenzylamine starting material

Table 1. *Selected geometric parameters (Å, °)*

C1′—C9	1.558 (4)	O1—C9	1.420 (4)
C2′—C7′	1.548 (5)	H19*b*···C3′	3.03
C7′—C8′	1.533 (6)	H19*b*···C4′	2.91
C7′—C9′	1.546 (5)	H21*c*···C5′	2.86
C7′—C10′	1.533 (6)	H21*c*···C6′	2.93
C1′—C9—C8a	112.2 (3)	C1′—C9—O1	110.9 (3)
C1′—C9—C9a	113.5 (3)		
C6′—C1′—C9—C9a	72.8 (4)	C7′—C2′—C1′—C6′	−176.3 (4)
C6′—C1′—C9—C8a	−40.4 (4)	C7′—C2′—C3′—C4′	178.1 (5)
C2′—C1′—C9—O1	18.6 (5)	C5′—C6′—C1′—C9	176.4 (4)
C6′—C1′—C9—O1	−160.6 (3)	C3′—C2′—C1′—C9	−175.0 (4)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*b*···O2^i	0.84 (4)	1.92 (4)	2.749 (4)	172 (5)
N1—H1*a*···O3	0.86	2.18	3.007 (6)	162

Symmetry code: (i) $1-x, y-\frac{1}{2}, -z$.

The H1*b* atom was refined isotropically; all other H atoms are riding.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS* and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*, *SHELXL*93 and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1426). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1016–1017

Chiral Bisphosphanes. IV.† Tetraisopropyl 2,2′-[(1*R*,2*R*)-Cyclopentane-1,2-diyl]bis-[(4*S*,5*S*)-1,3,2-dioxaphospholane-4,5-dicarboxylate]

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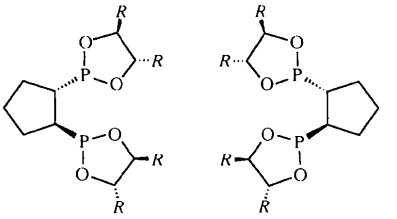
Abstract

The title compound, $C_{25}H_{40}O_{12}P_2$, was isolated in diastereomerically pure form from the reaction between *rac*,*trans*-$C_5H_8(PCl_2)_2$ and (2*S*,3*S*)-(−)-diisopropyl tartrate. The crystal structure determination reveals that the two P-bonded ring-C atoms have *R* configurations.

Comment

In previous work (Eckert *et al.*, 1995), we reported on the reaction between racemic *trans*-cyclopentane-1,2-diylbis(phosphonous dichloride) [*rac*,*trans*-$C_5H_8(PCl_2)_2$] and (2*R*,3*R*)-(+)-diisopropyl tartrate, giving 2,2′-(cyclopentane-1,2-diyl)bis(1,3,2-dioxaphospholane), *trans*-$C_5H_8[(^iPrO_2C)HC^{R}OPOC^{R}H(CO_2{}^iPr)]_2$, as a mixture of (1*S*,2*S*) and (1*R*,2*R*) diastereomers. Crystallization of the diastereomeric mixture from diethyl ether resulted in preferential precipitation of the (1*S*,2*S*) form, (I), as shown by X-ray structure analysis.



(I) (II)

A similar reaction employing (2*S*,3*S*)-(−)-diisopropyl tartrate as the diol component furnished the (1*S*,2*S*)- and (1*R*,2*R*)-configured epimers of *trans*-$C_5H_8[(^iPrO_2C)HC^{S}OPOC^{S}H(CO_2{}^iPr)]_2$, as expected. Fractional crystallization of the compound from diethyl ether afforded one of the two stereoisomers as well shaped transparent

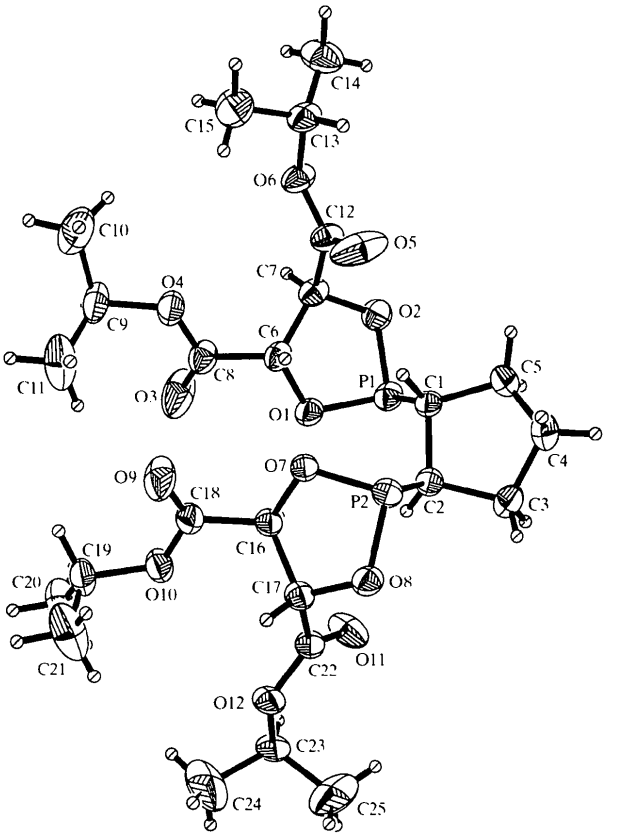


Fig. 1. The structure of the title molecule with displacement ellipsoids drawn at the 30% probability level.

† Part III: Dahlenburg & Kurth (1998).