C(1′)—C(2′)—C(3′)—O(3′)	−88.69 (68)
C(1′)—C(2′)—C(3′)—C(4′)	29.42 (72)
P—C(3′)—C(4′)—O(4′)	−161.83 (49)
P—C(3′)—C(4′)—C(5′)	75.95 (74)
P—C(3′)—C(4′)—H(4′)	−35.60 (375)
O(3′)—C(3′)—C(4′)—O(4′)	75.98 (69)
O(3′)—C(3′)—C(4′)—C(5′)	−46.23 (82)
O(3′)—C(3′)—C(4′)—H(4′)	−157.78 (372)
C(2′)—C(3′)—C(4′)—O(4′)	−38.71 (71)
C(2′)—C(3′)—C(4′)—C(5′)	−160.93 (63)
C(2′)—C(3′)—C(4′)—H(4′)	87.52 (374)
O(4′)—C(4′)—C(5′)—O(5′)	72.16 (72)
C(3′)—C(4′)—C(5′)—O(5′)	−169.02 (58)
H(4′)—C(4′)—C(5′)—O(5′)	−56.18 (394)

Nucleophilic addition of lithium diethyl phosphite to the sensitive 5′-*O*-trityl-3′-keto-thymidine resulted in a solid product. The product was recrystallized from a mixture of $CHCl_3$ and MeOH with < 1% EtOH. The mixture was heated in a closed vial until the solid disolved completely into solution, whereupon, it was allowed to cool slowly to room temperature. The container lid was then removed and the mixture allowed to stand for approximately 20 h. Clear tabular crystals were then apparent and no solvent remained.

The scan range was $(0.9 + 0.35\tan\theta)^\circ$, the scan speed 0.5–3.3° min^{-1}; the background count was 25% below and above the range, and the ratio of counting time for reflections to background was 2:1. The structure was determined by direct methods. The least-squares procedure refined all non-H atoms anisotropically except for the ethoxy group C atoms, the *para* C atoms of the phenyl groups and the solvent molecule C atoms. A C atom of one ethoxy group appeared to be disordered and was refined as C(11*A*) and C(11*B*) with equal occupancies of 0.5. All H atoms were included in the structure-factor calculations at fixed positions except H(4′), which was included in the least-squares refinement.

The absolute stereochemistry of the ribose ring was known in advance and so no attempt was made to determine absolute configuration from X-ray diffraction data. The scattering factors, f' and f'', were included in the structure-factor calculations. The anomalous scattering factor calculations were expected to be small and the values of R for the two enantiomorph model refinements were not significantly different. The parameters supplied are for the enantiomer which corresponds to the known absolute stereochemistry.

Computer programs used: *MolEN* (Fair, 1990); *ORTEP* (Johnson, 1965).

We thank the National Institutes of Health (GM-44986) for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, least-squares-planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71573 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1082]

References

Bender, S. L. & Moffett, K. K. (1992). *J. Org. Chem.* **57**, 1646–1647.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf-Nonius, Delft, The Netherlands.

Grouiller, A., Essadiq, H., Pacheco, H., Juntunen, S. & Chattopadhyaya, J. (1985). *Angew. Chem. Int. Ed. Engl.* **24**, 52–53.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Pérez-Pérez, M., San-Félix, A., Camarasa, M., Balzarini, J. & De Clercq, E. (1992). *Tetrahedron Lett.* **33**, 3029–3032.

Webb, T. R. (1988). *Tetrahedron Lett.* **29**, 3769–3772.

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(*E*)-1,3-Dibenzoyl-2-trifluoromethylpropene and 3-Benzoyl-6-phenyl-2,4-bis(trifluoromethyl)-2*H*-pyran-2-ol: Novel Products from the Oxidation of 1-Phenyl-4,4,4-trifluorobut-2-yn-1-ol with Active Manganese(IV) Oxide

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Abstract

Comparison of the two benzoyl groups attached to the ends of the propene chain reveals a slight shrinkage in the linking C—C bond when the group is conjugated to the propene double bond [1.490 (7) *cf.* 1.527 (6) Å for the unconjugated group]. However, this is not reflected in the double bond itself, which at 1.312 (7) Å is extremely short. In the substituted pyran, the benzoyl group has been forced out of conjugation by steric congestion [O=C—C=C 91.4 (8)°, linking C—C 1.521 (7) Å] but in this case too, even though the adjacent double bond is able to conjugate within the pyran ring, it still retains full double-bond character [1.328 (8) Å]. Intermolecular hydrogen bonds between the benzoyl O atom and the alcohol group [O—H 0.99 (6), H···O 1.80 (6), O···O 2.738 (6) Å, O—H···O 157 (6)°] link the pyran molecules into infinite chains along *a*.

Comment

The structure determinations reported herein form part of a general investigation of the reactions of alkynes containing the $CF_3C{\equiv}C$ grouping (Tajammal & Tipping, 1990). The reaction of the alcohol (1) with active MnO_2 was undertaken in an attempt to prepare the corresponding ketone (2); however, (2) proved susceptible to hydrolysis

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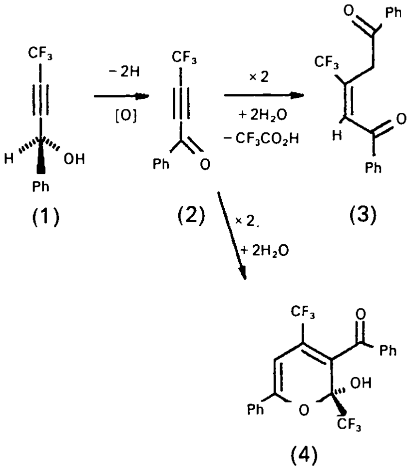
and gave (3) and (4), which were unexpected. The reaction pathway has been described fully by Tajammal & Tipping (1990) but may be summarized by the scheme below.



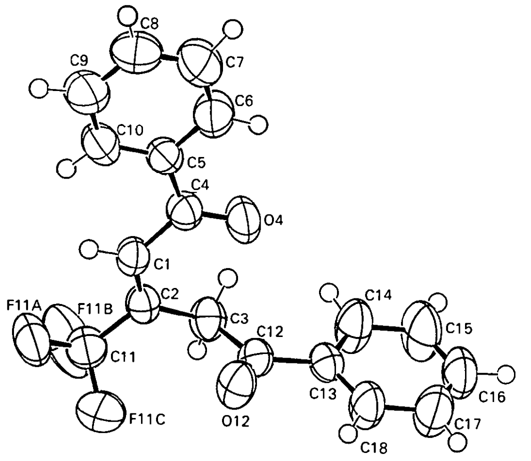


Fig. 1. Molecule (3), including atomic numbering scheme, drawn using *ORTEP*II (Johnson, 1976); the low-occupancy alternative fluorine conformation (F11*A*2, F11*B*2, F11*C*2) has been omitted for clarity.

Experimental

Compound (3)

Crystal data

$C_{18}H_{13}F_3O_2$
$M_r = 318.29$
Monoclinic
$C2/c$
$a = 37.941\ (8)$ Å
$b = 5.000\ (3)$ Å
$c = 18.454\ (2)$ Å
$\beta = 118.01\ (3)°$
$V = 3090\ (4)$ Å^3
$Z = 8$
$D_x = 1.368$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 8.09$–$13.09°$
$\mu = 0.1064$ mm^{-1}
$T = 296$ K
Plate
0.35 × 0.35 × 0.15 mm
Colourless

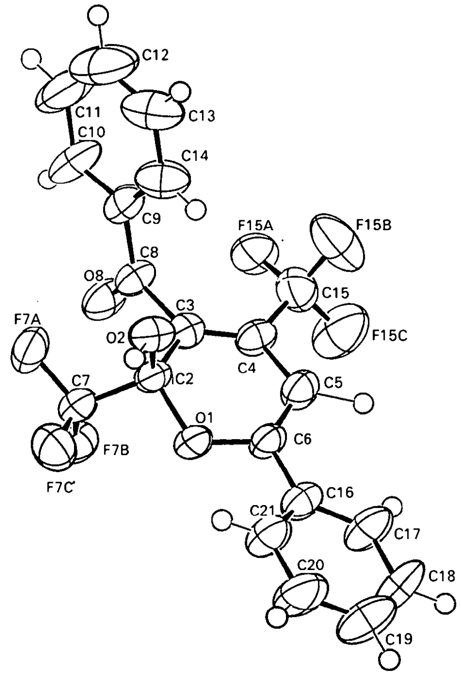


Fig. 2. Molecule (4), including atomic numbering scheme, drawn using *ORTEP*II (Johnson, 1976).

Data collection

CAD-4 diffractometer
ω scans
Absorption correction: none
2203 measured reflections
2153 independent reflections
1109 observed reflections [$I > 2.0\sigma(I)$]

$R_{\rm int} = 0.0126$
$\theta_{\rm max} = 23°$
$h = 0 \rightarrow 39$
$k = 0 \rightarrow 5$
$l = -18 \rightarrow 16$
3 standard reflections
frequency: 300 min
intensity variation: none

Refinement

Refinement on F
$R = 0.0431$
$wR = 0.0245$
$S = 2.461$
1109 reflections
268 parameters
All H-atom parameters refined
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{\rm max} = 0.0581$
$\Delta\rho_{\rm max} = 0.133$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.148$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for compound* (3)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
F11*A*	0.98409 (8)	0.3982 (7)	0.1587 (3)	0.0965
F11*B*	0.9624 (1)	0.0031 (7)	0.1358 (3)	0.1329
F11*C*	0.94534 (8)	0.2765 (10)	0.0387 (2)	0.1108
O4	0.85301 (7)	0.5651 (6)	0.1465 (2)	0.0824
O12	0.86335 (7)	0.5633 (6)	−0.0218 (2)	0.0740
C1	0.9204 (1)	0.5126 (10)	0.1792 (3)	0.0550
C2	0.9161 (1)	0.3319 (9)	0.1241 (3)	0.0522

C3	0.8779 (1)	0.188 (1)	0.0672 (3)	0.0615
C4	0.8877 (1)	0.6216 (9)	0.1937 (3)	0.0579
C5	0.8976 (1)	0.8072 (9)	0.2630 (3)	0.0539
C6	0.8666 (2)	0.901 (1)	0.2746 (3)	0.0815
C7	0.8733 (2)	1.078 (1)	0.3364 (4)	0.0962
C8	0.9109 (2)	1.165 (1)	0.3881 (3)	0.0852
C9	0.9421 (2)	1.073 (1)	0.3785 (3)	0.0945
C10	0.9353 (1)	0.892 (1)	0.3162 (3)	0.0791
C11	0.9517 (1)	0.250 (1)	0.1155 (3)	0.0682
C12	0.8507 (1)	0.3642 (10)	−0.0053 (2)	0.0532
C13	0.8084 (1)	0.2777 (9)	−0.0557 (3)	0.0523
C14	0.7905 (2)	0.082 (1)	−0.0337 (3)	0.0905
C15	0.7504 (2)	0.022 (1)	−0.0824 (4)	0.1109
C16	0.7290 (2)	0.157 (1)	−0.1521 (4)	0.0858
C17	0.7461 (2)	0.345 (1)	−0.1766 (3)	0.1010
C18	0.7859 (1)	0.408 (1)	−0.1275 (3)	0.0840
F11*A*2	0.977 (1)	0.14 (1)	0.188 (2)	0.05 (1)
F11*B*2	0.941 (1)	0.05 (1)	0.061 (2)	0.05 (1)
F11*C*2	0.966 (2)	0.439 (7)	0.098 (4)	0.05 (1)

Table 2. *Selected geometric parameters* (Å, °) *for compound* (3)

O4—C4	1.224 (4)	C2—C11	1.489 (8)
O12—C12	1.205 (6)	C3—C12	1.527 (6)
C1—C2	1.312 (7)	C4—C5	1.478 (6)
C1—C4	1.490 (7)	C12—C13	1.493 (5)
C2—C1—C4	125.5 (4)	O4—C4—C1	119.8 (4)
C1—C2—C3	126.5 (5)	O12—C12—C3	120.8 (3)
C2—C3—C12	111.6 (4)	C3—C12—C13	117.7 (4)

Compound (4)

Crystal data

$C_{20}H_{12}F_6O_3$
$M_r = 414.30$
Orthorhombic
$Pna2_1$
$a = 11.201\ (5)$ Å
$b = 19.601\ (4)$ Å
$c = 8.368\ (3)$ Å
$V = 1837\ (2)$ Å^3
$Z = 4$
$D_x = 1.498$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9.70$–$14.02°$
$\mu = 0.1332$ mm^{-1}
$T = 296$ K
Needle
0.40 × 0.20 × 0.20 mm
Colourless

Data collection

CAD-4 diffractometer
ω-2θ scans
Absorption correction: none
1915 measured reflections
1915 independent reflections
1304 observed reflections [$I > 2.0\sigma(I)$]

$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 13$
$k = -23 \rightarrow 0$
$l = -9 \rightarrow 0$
3 standard reflections
frequency: 300 min
intensity variation: none

Refinement

Refinement on F
$R = 0.0445$
$wR = 0.0393$
$S = 2.600$
1304 reflections
269 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.0328$

$\Delta\rho_{\max} = 0.166$ e Å^{-3}
$\Delta\rho_{\min} = -0.172$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
Absolute configuration: refinement of absolute structure unsuccessful, anomolous effect too small

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for compound* (4)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
F7*A*	0.1166 (3)	0.2939 (2)	0.7650	0.0697
F7*B*	−0.0114 (3)	0.2120 (2)	0.7473 (7)	0.0754
F7*C*	0.1741 (4)	0.1898 (2)	0.7876 (6)	0.0796
F15*A*	−0.1296 (3)	0.3372 (2)	0.2343 (7)	0.0699
F15*B*	−0.0124 (4)	0.3039 (2)	0.0506 (7)	0.1057
F15*C*	−0.1645 (4)	0.2427 (2)	0.1167 (7)	0.1062
O1	0.1115 (3)	0.1558 (2)	0.4978 (7)	0.0507
O2	0.2355 (4)	0.2508 (2)	0.4971 (7)	0.0544
O8	−0.0924 (4)	0.3420 (2)	0.5793 (7)	0.0628
C2	0.1226 (5)	0.2279 (2)	0.5304 (8)	0.0430
C3	0.0328 (5)	0.2696 (3)	0.4311 (9)	0.0431
C4	0.0000 (5)	0.2438 (3)	0.2910 (9)	0.0477
C5	0.0352 (6)	0.1772 (3)	0.2388 (10)	0.0540
C6	0.0887 (5)	0.1345 (3)	0.3439 (10)	0.0491
C7	0.0998 (7)	0.2298 (3)	0.7092 (9)	0.0590
C8	−0.0029 (5)	0.3390 (3)	0.4969 (9)	0.0467
C9	0.0691 (5)	0.4009 (3)	0.4603 (9)	0.0541
C10	0.0357 (6)	0.4603 (3)	0.530 (1)	0.0773
C11	0.1020 (10)	0.5201 (4)	0.494 (1)	0.1206
C12	0.1934 (9)	0.5176 (5)	0.392 (2)	0.1183
C13	0.2255 (8)	0.4560 (4)	0.324 (1)	0.0988
C14	0.1655 (6)	0.3976 (3)	0.358 (1)	0.0714
C15	−0.0760 (8)	0.2832 (4)	0.172 (1)	0.0729
C16	0.1235 (5)	0.0633 (3)	0.3182 (9)	0.0499
C17	0.0643 (5)	0.0240 (3)	0.204 (1)	0.0694
C18	0.0956 (7)	−0.0426 (3)	0.183 (1)	0.0888
C19	0.1819 (6)	−0.0728 (3)	0.274 (1)	0.0809
C20	0.2377 (7)	−0.0355 (3)	0.388 (1)	0.0884
C21	0.2060 (6)	0.0323 (3)	0.411 (1)	0.0645

Table 4. *Selected geometric parameters* (Å, °) *for compound* (4)

O1—C2	1.444 (6)	C2—C3	1.540 (8)
O1—C6	1.378 (7)	C3—C4	1.328 (8)
O2—C2	1.370 (6)	C4—C5	1.433 (7)
O8—C8	1.218 (6)	C5—C6	1.353 (8)
C2—O1—C6	119.3 (4)	C4—C3—C8	126.0 (5)
O1—C2—O2	111.2 (4)	C3—C4—C5	122.7 (6)
O1—C2—C3	111.2 (4)	C4—C5—C6	119.2 (6)
C2—C3—C4	117.0 (5)	O1—C6—C5	120.2 (5)

A mixture of 1-phenyl-4,4,4-trifluorobut-2-yn-1-ol (1) (0.80 g, 4.0 mmol) and active manganese(IV) oxide (4.10 g, 45.8 mmol) in dichloromethane (45 ml) was stirred under N_2 at room temperature for 24 h. Filtration and removal of the solvent from the filtrate *in vacuo* gave a residue (0.73 g) which was shown by TLC [eluant CH_2Cl_2/n-C_5H_{12} (2:1 *v*/*v*)] to contain two components (R_F 0.80 and 0.37). The components were separated by dry-column flash chromatography (silica Kieselgel 60H; same eluant) to give (i) (*E*)-1,3-dibenzoyl-2-trifluoromethylpropene (3) (0.15 g, 0.48 mmol, 24%; found C 67.7, H 4.0, F 18.1%, M^+ 318; $C_{18}H_{13}F_3O_2$ requires C 67.9, H 4.1, F 17.9%, *M* 318; m.p. 349 K) and (ii) 3-benzoyl-2-hydroxy-6-phenyl-2,4-bis(trifluoromethyl)-α-pyran (4) (0.54 g, 1.30 mmol, 65%; found C 58.3, H 3.1, F 27.7%, M^+ 414; $C_{20}H_{12}F_6O_3$ requires C 58.0, H 2.9, F 27.5%, *M* 414; m.p. 397 K). Compound (3) was recrystallized from *n*-pentane and compound (4) from *n*-pentane/$CHCl_3$ (10:1 *v*/*v*).

For both compounds: data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*

LS. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*. Literature search: *CSSR* (1984).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71596 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1059]

References

CSSR (1984). *Crystal Structure Search and Retrieval Instruction Manual*. SERC Daresbury Laboratory, Warrington, England.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1985). *SHELXS86*. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175-189. Oxford Univ. Press.

Tajammal, S. & Tipping, A. E. (1990). *J. Fluorine Chem.* **47**, 45-57.

Acta Cryst. (1994). C**50**, 297–300

Structures of *ap*-8-Bromo-1,4-dimethyl-9-(2-methylbenzyl)triptycene and *sc**(9*S**)-8-Bromo-1,4-dimethyl-9-(2-methylbenzyl)triptycene

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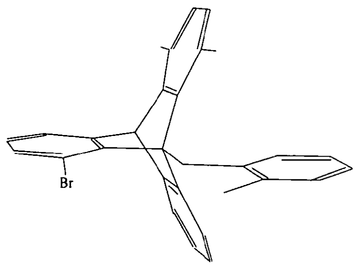
(*Received* 23 *March* 1993; *accepted* 9 *August* 1993)

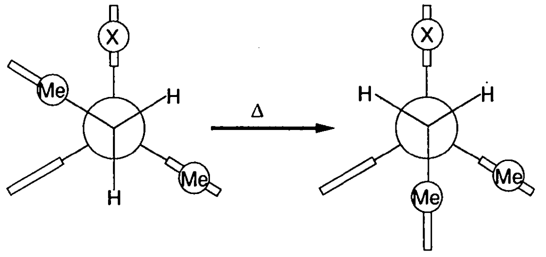
Abstract

Two atropisomers, *ap* and *sc**(9*S**), of the title compound [8-bromo-1,4-dimethyl-9-(2-methylbenzyl)-9,10-dihydro-9,10-*o*-benzenoanthracene, $C_{30}H_{25}Br$] have been isolated and their structures determined by X-ray diffraction. The molecular structures confirm those assumed by NMR study. The crystal of the *sc**(9*S**) isomer decomposed during the transition to the *ap* form at 457.3 K, probably because the two crystal structures are quite different to each other.

Comment

Atropisomerism is defined as stereoisomerism due to restricted rotation about single bonds where the isomers can actually be isolated (Eliel, 1962). Several examples of atropisomerism have been found in 9-substituted triptycene derivatives (Iwamura, 1973; Yamamoto & Oki, 1975; Otsuka, Yamamoto, Mitsuhashi & Oki, 1979; Otsuka, Mitsuhashi & Oki, 1980; Yamamoto, Suzuki & Oki, 1981; Yonemoto, Kakizaki, Yamamoto, Nakamura & Oki, 1985; Tanaka, Yonemoto, Nakai, Yamamoto & Oki, 1988; Oki, Tanuma, Tanaka & Yamamoto, 1988). Recently 8-chloro- and 8-bromo-1,4-dimethyl-9-(2-methylbenzyl)triptycene were synthesized (Yamamoto, 1990, 1991). These compounds have three rotational isomers, *ap*, *sc**(9*S**) and *sc**(9*R**), as shown below. The *sc**(9*R**) form may be less stable since the 2-methylphenyl group lies between two *peri* substituents. From the NMR study, the isolated isomers were assumed to be the *ap* and *sc**(9*S**) forms. The differential scanning calorimetry (DSC) measurements performed when the *sc**(9*S**) isomer was heated, produced a weak broad endothermic peak at 457.3 K and then a sharp exothermic peak due to melting at 533.5 K. The endothermic peak was assigned to the transition from the *sc**(9*S**) isomer to the *ap* form by NMR measurements. Since no change in appearance of the crystalline samples was observed during the transition, it was assumed that the transition may occur with retention of the crystal form (Yamamoto, Nemoto & Ohashi, 1992). The molecular structures shown in Fig. 1 confirm those assumed by NMR





sc
Isomer (II)

ap
Isomer (I)

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