O4—S2—O3	119.76 (9)	C2—C1—N1	113.99 (15)
O4—S2—N1	109.97 (8)	C2—C1—C6	112.6 (2)
O3—S2—N1	105.52 (8)	N1—C1—C6	112.55 (15)

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1049). Services for accessing these data are described at the back of the journal.

References

Blaschette, A., Naveke, M. & Jones, P. G. (1991). *Z. Naturforsch. Teil B*, **46**, 5–14.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. *Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Curtis, V. A., Knutson, F. J. & Baumgarten, R. J. (1981). *Tetrahedron Lett.* **22**, 199–202.

Curtis, V. A. & Pavkovic, S. F. (1983). *Acta Cryst.* C**39**, 1077–1078.

Henschel, D., Blaschette, A. & Jones, P. G. (1997). *Acta Cryst.* C**53**, 1669–1671.

Jones, P. G., Hamann, T., Schaper, W., Lange, I. & Blaschette, A. (1995). *Phosphorus Sulfur Silicon*, **106**, 91–104.

Pavkovic, S. F., Wilhelm, F. C. & Brown, J. N. (1978). *Acta Cryst.* B**34**, 1337–1340.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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ap-9-(*o*-*tert*-Butylphenyl)-9-methylthiofluorene, the first isolated *ap* rotamer of a 9-substituted 9-(*o*-*tert*-butylphenyl)fluorene

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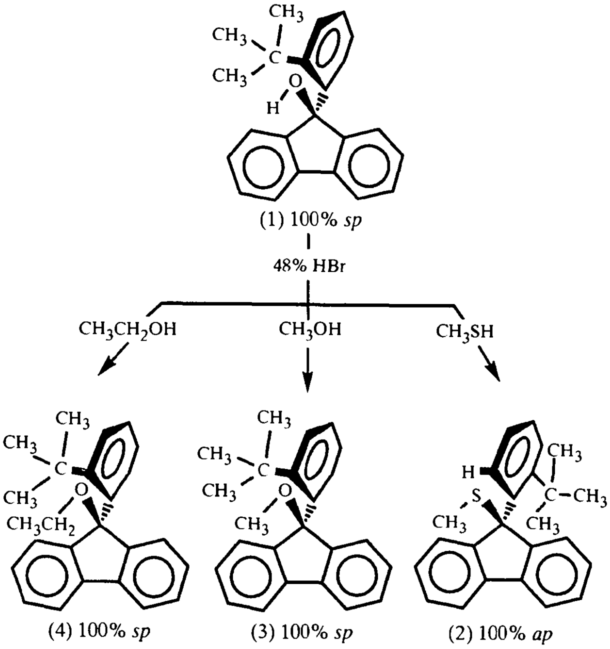
Abstract

Treatment of *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenol with HBr and methanethiol provided *ap*-9-(*o*-*tert*-butylphenyl)-9-methylthiofluorene, $C_{24}H_{24}S$, exclusively, the first isolated *ap* rotamer of a 9-substituted 9-(*o*-*tert*-butylphenyl)fluorene. The *ap* configuration in this series, generally the thermodynamically less favored, is preferred in the case of the title compound because the even larger interaction between the *tert*-butyl group and S in the *sp* configuration is energetically forbidden. The extensive distortion in the title compound is obvious from its X-ray structure and the associated geometric parameters.

Comment

As part of our recent studies of rotationally restricted 9-substituted fluorenes (Hou, 1997), we prepared 9-(*o*-*tert*-butylphenyl)-9-methylthiofluorene, (2). We found that, while 9-(*o*-*tert*-butylphenyl)-9-fluorenol, (1), 9-(*o*-*tert*-butylphenyl)-9-methoxyfluorene, (3), and 9-(*o*-*tert*-butylphenyl)-9-ethoxyfluorene, (4), exist solely in their *sp* configurations, (2) exists exclusively in its *ap* configuration, both in solution and in its crystalline state (Meyers *et al.*, 1997; Robinson *et al.*, 1998). The strong steric repulsion between the *tert*-butyl group and the fluorene π cloud makes the *ap* configuration highly unstable (Nakamura *et al.*, 1977; Ōki, 1993; Meyers *et al.*, 1995, 1997). Our finding that the *ap* configuration of (2) is the exclusive form tells us that the 9-methylthio group enforces the *ap* configuration which, although highly energetic *per se*, is nonetheless thermodynamically favored over the *sp* configuration in this case. Compound (2) is the first isolated *ap* rotamer of a 9-substituted 9-(*o*-*tert*-butylphenyl)fluorene.



The extensive distortions in *ap* (2) are displayed in its X-ray structure, which is shown in Fig. 1 with the atom-numbering scheme. The selected geometric parameters compared in Table 1 clearly illustrate the strain in (2). This strain accounts for its unusual instability, which leads to its facile homolytic decomposition at room temperature, in contrast to the thermal stability

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of the *sp* compounds, *e.g.* (1), (3) and (4) (Meyers *et al.*, 1997). The fact that (2) exists solely in its *ap* configuration in solution, as shown by NMR spectroscopy, signifies that its distortions emanate from its intrinsic molecular structure. Packing is not a factor, the shortest intermolecular distance being 3.554 (3) Å, between two C4 atoms of adjacent molecules. The major source of the strain emanates from the methyl C10′ impinging on the face of the fluorene ring, evidenced by its extreme proximity to C9a. As a result, the bond between the *tert*-butyl group and phenyl, C2′—C7′, is considerably bent, the C1′—C2′—C7′ angle being over 17° larger than the corresponding C3′—C2′—C7′ angle. In turn, the C2′—C7′—C10′ angle is greatly distorted relative to the corresponding angles, C2′—C7′—C9′ and C2′—C7′—C8′. For the same reason, the bond between the phenyl and fluorene rings, C1′—C9, is bent, making the C2′—C1′—C9 angle some 13° larger than the corresponding C6′—C1′—C9 angle and forcing the S1—C9 bond more towards perpendicularity with the fluorene plane [the angle between the S1—C9 vector and the fluorene ring plane is 99.09 (7)°]. The magnitude of this distortion is further illustrated by the fact that the C4b—C8a—C9—C1′ torsion angle is almost 53° larger than that of S1—C9—C9a—C4a. The 9-phenyl ring itself is unusually distorted compared with the fluorene phenyl rings; for example, the average deviation of the atoms from the C1′–C6′ least-squares plane is 0.028 (2) Å, while equivalent values for the C1–C9a and C4b–C8a phenyl rings are 0.010 (2) and 0.005 (2) Å, respectively.

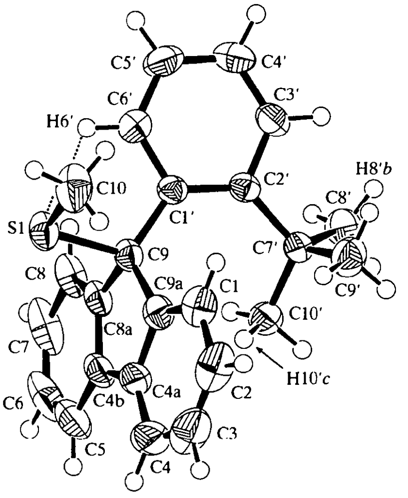

Fig. 1. The molecular structure and atom-numbering scheme for (2), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of an arbitrary radius.

The molecular distortion results in unusually intimate intramolecular non-bonding contacts, *e.g.* C9a···C10′, C1···C10, C9a···H10′*c*, C3′···H8*b*′ and C4a···H10′*c*, all of whose distances are smaller than the sum of their respective van der Waals radii. In this regard, the very close contact of S1···H6′ might be considered a 'hydrogen bond', the S1···C6′ distance being only 2.961 (2) Å and the ^{1}H NMR resonance of H6′ (*ca* δ 9.0) being very much deshielded compared with normal aromatic H resonances (Hou, 1997; Meyers *et al.*, 1997).

Experimental

To prepare *ap* (2), precooled 48% HBr was added to a mixture of *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenol (Robinson *et al.*, 1998; Nakamura *et al.*, 1977) and methanethiol. The mixture was maintained at 258 K overnight; the residual methanethiol was then evaporated, the residue extracted with hexanes, and the combined extracts washed with water, dilute aqueous $NaHCO_3$ solution, and water again. Rotary evaporation left a light yellow solid [*ca* 100% yield; m.p. 383–386.5 K (decomposed with bubbling, gas possibly MeSSMe; color deepens at 363 K)]. ^{1}H and ^{13}C NMR showed a single product and supported its general structure as *ap*-9-(*o*-*tert*-butylphenyl)-9-methylthiofluorene, (2). Recrystallization from hexanes provided crystals suitable for X-ray analysis, which unequivocally confirmed its structure as *ap* (2).

Crystal data

$C_{24}H_{24}S$
M_r = 344.49
Monoclinic
$P2_1/c$
a = 12.014 (6) Å
b = 9.800 (2) Å
c = 16.068 (3) Å
β = 93.80 (3)°
V = 1887.7 (11) Å^3
Z = 4
D_x = 1.212 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 12.6–13.5°
μ = 0.174 mm^{-1}
T = 296 K
Equant fragment
0.49 × 0.46 × 0.43 mm
Pale purple

Data collection

Rigaku AFC-5*S* diffractometer
ω scans (6° min^{-1} in ω)
Absorption correction: none
6671 measured reflections
3338 independent reflections
2291 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.038
$\theta_{\rm max}$ = 25°
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 11$
$l = -19 \rightarrow 19$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.036
$wR(F^2)$ = 0.102
S = 1.00
3338 reflections
230 parameters
H-atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.2687P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max}$ = 0.007
$\Delta\rho_{\rm max}$ = 0.17 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.17 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—C9	1.8872 (19)	S1—C10	1.798 (2)
C1′—C2′	1.423 (2)	C1′—C6′	1.400 (3)
C2′—C3′	1.405 (2)	C3′—C4′	1.369 (3)
C4′—C5′	1.361 (3)	C5′—C6′	1.367 (3)
C1···C10	3.273 (4)	C9a···C10′	3.145 (3)
C3′···H8*b*′	2.58	C9a···H10*c*′	2.35
C4a···H10*c*′	2.50		
C1′—C2′—C7′	130.98 (15)	C3′—C2′—C7′	113.63 (16)
C2′—C1′—C9	128.01 (16)	C6′—C1′—C9	114.94 (15)
C1′—C9—C8a	115.67 (14)	C1′—C9—C9a	121.83 (14)
S1—C9—C9a	101.70 (11)	S1—C9—C8a	99.44 (11)
C2′—C7′—C10′	115.52 (14)	C2′—C7′—C8′	109.26 (15)
C2′—C7′—C9′	109.93 (15)		
S1—C9—C9a—C4a	91.53 (15)		
C4b—C8a—C9—C1′	143.98 (15)		

The rotation of the methyl H atoms were refined by the circular difference electron density method available in *SHELXL*97 (Sheldrick, 1997). All H atoms are riding.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL*97. Molecular graphics: *TEXSAN* and *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*, *SHELXL*97 and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1440). Services for accessing these data are described at the back of the journal.

References

Hou, Y. (1997). PhD Dissertation. Southern Illinois University, Carbondale, Illinois, USA.

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

Meyers, C. Y., Hou, Y., Lutfi, H. G. & Robinson, P. D. (1995). *Am. Chem. Soc. Natl Meet.*, Chicago, August, Abstract ORGN 297.

Meyers, C. Y., Hou, Y., Lutfi, H. G., Robinson, P. D., Dunn, H. E. & Seyler, J. W. (1997). *Am. Chem. Soc. Natl Meet.*, San Francisco, April, Abstract ORGN 351.

Molecular Structure Corporation (1996). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1997). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Nakamura, M., Nakamura, N. & Ōki, M. (1977). *Bull. Chem. Soc. Jpn*, **50**, 2986–2990.

Ōki, M. (1993). *The Chemistry of Rotational Isomers* (ch. 3), Vol. 30 of *Reactivity and Structure Concepts in Organic Chemistry*, edited by K. Hafner, J.-M. Kehn, C. W. Rees, P. v. R. Schleyer, B. M. Trost & R. Zahradník. New York: Springer-Verlag.

Robinson, P. D., Hou, Y., Lutfi, H. G. & Meyers, C. Y. (1998). *Acta Cryst.* C**54**, 73–77.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

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2,2′-Dibromobiphenyl

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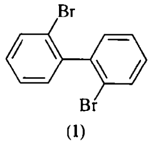
Abstract

The title compound, $C_{12}H_8Br_2$, crystallizes in the orthorhombic space group *Pbca*. The molecule displays non-planar behaviour and the dihedral angle between the two six-membered rings is 84.8 (2)°. The bond length between the two phenyl rings (C1—C1′) and the C—Br bond lengths (C2—Br1 and C2′—Br2) are 1.499 (9), 1.895 (8) and 1.915 (7) Å, respectively.

Comment

The biphenyl system has been extensively studied by X-ray crystallography. Of particular interest in relation to bonding theory is the length of the inter-ring C—C bond and the interplanar dihedral angle. Furthermore, the inter-ring torsion angle has been correlated to the toxicities of polychlorinated biphenyls (PCBs) (Miao *et al.*, 1996) and also crystal-packing effects (Brock & Minton, 1989). Most crystal structures in the literature have inter-ring angles in the rather limited range of 30–60° and only *ortho*-substituted biphenyls display larger angles. We report now the crystal structure of 2,2′-dibromobiphenyl, (I), to provide further structural data for biphenyls having larger inter-ring angles, and as part of our studies of *ortho*-substituted biphenyls.



(I)

The C—C bond distances within the phenyl rings in the title compound are normal and range from 1.365 (11) to 1.402 (9) Å with a mean of 1.378 Å. The corresponding bond angles range from 116.7 (7) to 122.9 (7)°. The phenyl rings are planar, but the Br1 and Br2 atoms