

O5—C4—C6	109.8 (2)	O25—C24—C23	108.5
C3—C4—C6	108.2 (2)	C26—C24—C23	112.76 (9)
C8—C4—C6	113.5 (2)	C27—C26—C24	121.05 (16)
C7—C6—C4	115.0 (3)	C31—C26—C24	118.91 (16)
C9—C8—C13	120.0		
O5—C4—C8—C9	34.2 (2)	C3—C4—C8—C9	-80.43 (19)
O22—C23—C24—C26	-115.15 (11)	N2—C3—C4—C6	-107.9 (3)
O22—C23—C24—O25	7.1 (2)	C3—C4—C6—C7	61.2 (3)
C23—C24—C26—C27	38.69 (16)	N2—C3—C4—O5	9.0 (4)
N2—C3—C4—C8	128.1 (3)		

Table 4. Hydrogen-bonding geometry (Å, °) for (II)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1A...O22	0.87 (4)	2.01 (4)	2.810 (3)	153 (3)
N1—H1B...O25 <sup>a</sup>	0.88 (4)	2.04 (4)	2.869 (3)	159 (3)
N2—H2A...O21	0.94 (5)	1.85 (5)	2.784 (3)	175 (4)
N2—H2B...O5	0.89 (4)	1.98 (4)	2.504 (3)	116 (4)
O5—H5A...O21 <sup>a</sup>	0.71 (4)	1.97 (5)	2.675 (3)	176 (5)
O25—H25A...O22	0.89	1.89	2.535 (2)	128.3

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

For both compounds, data collection: *CAD-4/PC* (Enraf-Nonius, 1993); cell refinement: *CAD-4/PC*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structures: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997b); molecular graphics: *PLATON92* (Spek, 1992a) and *PLUTON92* (Spek, 1992b); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1392). Services for accessing these data are described at the back of the journal.

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## *sp*-9-[*o*-(β-Chloro-α,α-dimethylethyl)-phenyl]fluorene: an Unanticipated Exclusive Product from the Reaction of *sp*-9-(*o*-*tert*-Butylphenyl)-9-fluorenol with Thionyl Chloride

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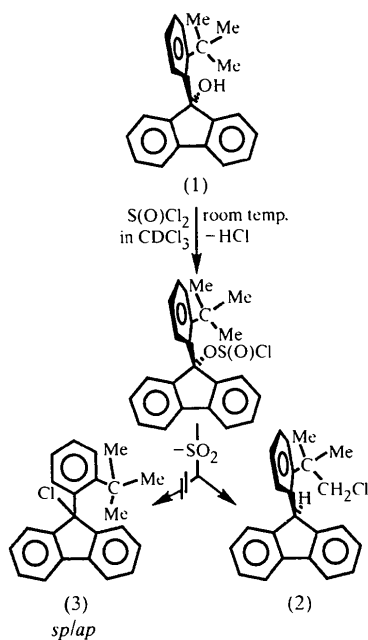
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## Abstract

The reaction of *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenol, (1), with thionyl chloride in CHCl<sub>3</sub> at room temperature quantitatively provided the title compound [(2), C<sub>23</sub>H<sub>21</sub>Cl], instead of the expected 9-(*o*-*tert*-butylphenyl)-9-chlorofluorene. Chlorination of an alkyl group under the conditions in which (1) was converted into (2) is apparently unprecedented. While the unexpected structure of (2) was suggested by <sup>1</sup>H and <sup>13</sup>C NMR, unequivocal characterization required X-ray crystallographic analysis. Surprisingly, introduction of the Cl atom in (2) imposes only a few minor changes in the bonding parameters compared with its non-chlorinated counterpart, *sp*-9-(*o*-*tert*-butylphenyl)fluorene.

## Comment

Thionyl chloride is the commonly used reagent in the classical conversion of an alcohol into its alkyl chloride, presumably through the S<sub>N</sub>i mechanism (Schreiner *et al.*, 1993). Accordingly, in our plan to convert *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenol [(1); Robinson *et al.*, 1998; Nakamura *et al.*, 1977] into the corresponding 9-(*o*-*tert*-butylphenyl)-9-chlorofluorene, (3), to determine whether it would be the *ap* or *sp* rotamer, or both (Meyers *et al.*, 1997), we treated (1) with SOCl<sub>2</sub> in the usual manner (see Scheme below). The colorless crystalline product had the molecular formula of the desired product and a sharp melting point, and was isolated in quantitative yield, but its <sup>1</sup>H and <sup>13</sup>C NMR spectra were incorrect for compound (3). The presence of a singlet for a CH<sub>2</sub> group together with a singlet representing two identical CH<sub>3</sub> groups suggested that the *tert*-butyl group had been monochlorinated. Such a transformation under these conditions was unprecedented. An X-ray diffraction study was thus undertaken to verify the structure.



The X-ray crystal structure of the product, shown with the atom numbering in Fig. 1, unequivocally identified it as *sp*-9-[*o*-( $\beta$ -chloro- $\alpha,\alpha$ -dimethylethyl)phenyl]fluorene, (2). Indeed, the *tert*-butyl group of (1) was monochlorinated and the 9-OH group was replaced by a H atom. A comparison of selected bond parameters of (2) with those of its non-chlorinated counterpart, *sp*-9-(*o*-*tert*-butylphenyl)fluorene (Robinson *et al.*, 1998), shows that substitution of a Cl atom in the *tert*-butyl

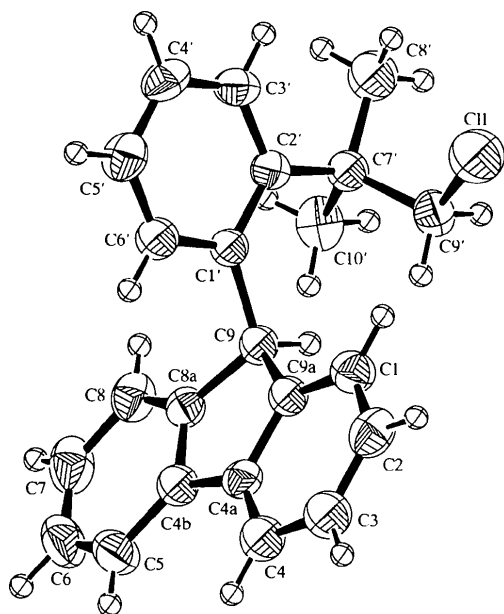


Fig. 1. The molecular structure and atom-numbering scheme for (2), with displacement ellipsoids at the 50% probability level.

group imparts surprisingly little change to the crystal structure. The near perpendicularity of the phenyl and fluorenyl rings is maintained, the angle between their least-squares planes in (2) being 88.58(7)°. While it might reasonably be expected that the angular distortion imposed by the proximity of the *tert*-butyl group to the fluorene ring would be increased by the chlorine substitution, the angles in question are essentially unchanged. Selected geometric parameters are given in Table 1.

## Experimental

For the preparation of compound (2), freshly distilled thionyl chloride (6 drops, *ca* 0.02 ml, 0.27 mmol) was added to an NMR tube containing a colorless solution of (1) (27.4 mg, 0.087 mmol) in *ca* 0.5 ml of CDCl<sub>3</sub>. The tube was shaken thoroughly and then allowed to stand. Most of the starting material was consumed within 25 min, as indicated by the absence of its OH resonance in a <sup>1</sup>H NMR spectrum of the colorless solution. Small broad resonances soon appeared at  $\delta$  0.83 and 8.70, the former eventually splitting into a sharp peak at  $\delta$  0.77 and a broad resonance at 0.84. After several hours, three prominent singlets were exhibited,  $\delta$  1.81, 4.16 and 5.65 in a ratio of 6:2:1, suggesting two CH<sub>3</sub> groups, CH<sub>2</sub>:Cl and fluorene H9, respectively. The solvent was removed *via* rotary evaporation leaving a light-yellow oil (yield: 28.5 mg, 98.5%); addition of hexanes provided the white crystals of (2) [m.p. 449.5–451 K (corr.)] used in the X-ray study. NMR: <sup>1</sup>H (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.81 (*s*, 6H), 4.16 (*s*, 2H), 5.65 (*s*, 1H), 6.25 (*dd*,  $J_{5'6'} = 7.8$ ,  $J_{4'6'} = 1.5$  Hz, 1H), 6.93 (*ddd*,  $J_{5'6'} = 7.8$ ,  $J_{4'5'} = 7.2$ ,  $J_{3'5'} = 1.2$  Hz, 1H), 7.15 (*ddd*,  $J_{3'4'} = 8.1$ ,  $J_{5'6'} = 7.2$ ,  $J_{4'6'} = 1.5$  Hz, 1H), 7.25 (*m*,  $J = 7.8, 1.2, 0.9$  Hz, 4H), 7.39 (*m*,  $J_{34,56} = 7.8$  Hz, 2H), 7.45 (*dd*,  $J_{3'4'} = 8.1$ ,  $J_{3'5'} = 1.2$  Hz, 1H), 7.83 (*d*,  $J_{34,56} = 7.8$  Hz, 2H). <sup>13</sup>C (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 26.67, 40.98, 51.08, 55.76, 119.93, 125.09, 126.47, 127.26, 127.30, 127.44, 127.57, 131.18, 139.88, 141.02, 143.20, 149.48. IR (Nujol mull): 3061 (*w*), 2953 (*s*), 1486 (*m*), 764 (*m*), 743 (*s*), 724 (*m*) cm<sup>-1</sup>.

### Crystal data

C<sub>23</sub>H<sub>21</sub>Cl

$M_r = 332.87$

Triclinic

$P\bar{1}$

$a = 9.0116(17)$  Å

$b = 12.073(3)$  Å

$c = 8.4305(18)$  Å

$\alpha = 104.542(19)^\circ$

$\beta = 96.133(17)^\circ$

$\gamma = 86.504(18)^\circ$

$V = 882.2(3)$  Å<sup>3</sup>

$Z = 2$

$D_x = 1.253$  Mg m<sup>-3</sup>

$D_m$  not measured

Mo K $\alpha$  radiation

$\lambda = 0.71069$  Å

Cell parameters from 25

reflections

$\theta = 12.7\text{--}17.5^\circ$

$\mu = 0.217$  mm<sup>-1</sup>

$T = 296$  K

Prism

$0.38 \times 0.35 \times 0.34$  mm

Colorless

### Data collection

Rigaku AFC-5S diffractometer

$R_{int} = 0.026$

$\theta_{max} = 25^\circ$

$\omega/2\theta$  scans (rate:  $6^\circ \text{ min}^{-1}$   
in  $\omega$ )  
Absorption correction: none  
6224 measured reflections  
3112 independent reflections  
2142 reflections with  
 $I > 2\sigma(I)$

#### Refinement

Refinement on  $F^2$   
 $R(F) = 0.035$   
 $wR(F^2) = 0.094$   
 $S = 1.008$   
3112 reflections  
220 parameters  
H atoms riding  
 $w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.1931P]$   
where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.154 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.195 \text{ e } \text{Å}^{-3}$   
Extinction correction:  
*SHELXL97*  
Extinction coefficient:  
0.030 (3)  
Scattering factors from  
*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ )

C11—C9'	1.792 (2)	C7'—C9'	1.535 (3)
C1'—C9	1.528 (2)	C7'—C8'	1.540 (3)
C2'—C7'	1.542 (2)	C7'—C10'	1.549 (3)
C1'—C2'—C7'	124.25 (15)	C6'—C1'—C9	115.04 (15)
C3'—C2'—C7'	119.13 (16)	C9'—C7'—C10'	108.03 (16)
C2'—C1'—C9	125.76 (15)	C9'—C7'—C8'	107.43 (15)
C4b—C8a—C9—C1'	-126.03 (16)	C9—C1'—C2'—C7'	5.2 (3)
C8—C8a—C9—C1'	56.6 (2)	C9—C1'—C6'—C5'	176.66 (17)
C1'—C9—C9a—C1	-54.2 (2)	C6'—C1'—C2'—C3'	2.2 (2)

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985) in *TEXSAN*. Program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP* (Johnson, 1965) in *TEXSAN*. Software used to prepare material for publication: *TEXSAN*, *SHELXL97* and *PLATON* (Spek, 1990).

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### 3,4-Bis(1-adamantyl)-1,2-dithiete: the First Structurally Characterized Dithiete Unsupported by a Ring or Benzenoid Frame

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#### Abstract

The structure determination of 3,4-bis(1-adamantyl)-1,2-dithiete,  $(\text{C}_{10}\text{H}_{15})_2\text{C}_2\text{S}_2$  or  $\text{C}_{22}\text{H}_{30}\text{S}_2$ , reported herein is the first crystallographic characterization of a 1,2-dithiete molecule unsupported by a benzenoid frame. Two independent molecules exist in the asymmetric unit separated by a pseudo-inversion center. The  $\text{S}_2\text{C}_2$  four-membered dithiete ring is planar, with a trapezoidal shape enforced by the longer disulfide bond [average  $2.086(2) \text{ Å}$ ] compared with the olefinic bond [average  $1.363(6) \text{ Å}$ ]. The adamantyl substituents differ from one another by adopting slightly different rotational conformations with respect to the dithiete ring. The quaternary C atoms of the adamantyl groups deviate only slightly from the plane of the dithiete ring (average displacement of  $0.023 \text{ Å}$ ).

#### Comment

1,2-Dithietes and their valence tautomers, the  $\alpha$ -dithiones (see scheme below), have long been known to add oxidatively to low-valent transition metal compounds to form redox-active bis- or tris(dithiolene) metal complexes  $[M(\text{S}_2\text{C}_2\text{R}_2)_{2,3}]^{\pm}$ , many examples of