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A Chromotropic Bi(benzofuranonyl)

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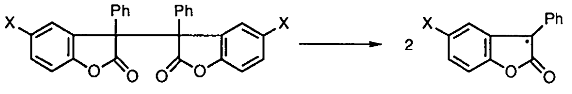
Abstract

The structure of a chromotropic compound, 5,5′-dichloro-3,3′-diphenyl-3,3′-bi(1-benzofuran)-2,2′-(3*H*,3′*H*)-dione (I), $C_{28}H_{16}Cl_2O_4$, has been determined. The C(3)—C(3′) bond, which undergoes homolysis by mechanical energy such as rubbing, is lengthened to 1.624 (4) Å compared with the average hexa-substituted C_{sp^3}—C_{sp^3} bond length. In the crystal, the molecule exists in a nonsymmetric *gauche* conformation.

Comment

3,3′-Diphenyl-3,3′-bi(1-benzofuran)-2,2′(3*H*,3′*H*)-dione (II) was reported to exhibit piezochromism† in the solid state (Löwenbein & Schmitt, 1927). Recently it was revealed that this mechanochromic phenomenon was responsible for the reversible cleavage of the C(3)—C(3′) bond to give blue-coloured benzofuranonyl radicals (Watanabe, 1987). There have been few reports on organic mechanochromic compounds and investigations from the structural chemistry viewpoint are very limited (Ohkanda, Mori, Maeda & Osawa, 1992) since these compounds were obtained only as powdery solids.



(I) $X = Cl$
(II) $X = H$

Compound (I), the 5-chloro derivative of (II), also exhibited mechanochromism and gave a single crystal suitable for X-ray structure analysis. The C(3)—C(3′) bond is lengthened to 1.624 (4) Å compared with the average length (1.588 Å) of hexa-substituted C_{sp^3}—C_{sp^3} bonds (Allen *et al.*, 1987). This bond elongation seems to be caused by steric repulsion and through-bond interactions between the phenyl groups at the 3 and 3′ positions. In the crystal, the molecule is not in a centrosymmetric *anti* conformation but is instead in a nonsymmetric *gauche* conformation (Fig. 2). The corresponding bond angles around C(3) and C(3′) are somewhat different from each other, while bond distances and other angles of the two halves of the molecule coincide within experimental error.

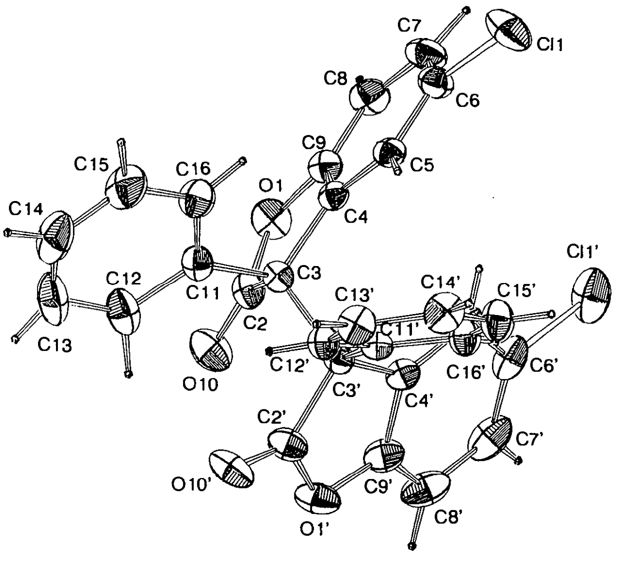


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title molecule with the atomic numbering scheme. The displacement ellipsoids for non-H atoms enclose 30% probability.

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† We proposed a term 'mechanochromism' instead of piezochromism based on the fact that the mechanochemical reaction is caused by rubbing rather than high pressure (Ohkanda, Mori, Maeda & Osawa, 1992).

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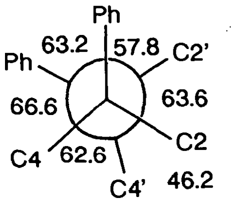

Fig. 2. Newmann projection about the C(3)—C(3′) bond and associated torsion angles (°).

Experimental

Compound (I) was synthesized by the method of Löwenbein & Schmitt (1927). Recrystallization was carried out from benzene-ethanol.

Crystal data

$C_{28}H_{16}Cl_2O_4$
$M_r = 487.3$
Monoclinic
$P2_1/n$
$a = 12.250\ (4)$ Å
$b = 20.420\ (8)$ Å
$c = 9.633\ (4)$ Å
$\beta = 108.24\ (3)°$
$V = 2288.5\ (16)$ Å^3
$Z = 4$

$D_x = 1.414$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 18 reflections
$\theta = 12.5$-$15.0°$
$\mu = 0.32$ mm^{-1}
$T = 294$ K
Plate
0.5 × 0.4 × 0.4 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer
ω-2θ scans
Absorption correction: none
4284 measured reflections
3567 independent reflections
2864 observed reflections $[F_o > 3\sigma(F_o)]$

$R_{\rm int} = 0.021$
$\theta_{\max} = 25.0°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 11$
3 standard reflections monitored every 50 reflections intensity variation: <3.0%

Refinement

Refinement on F
$R = 0.049$
$wR = 0.055$
$S = 1.835$
2864 reflections
371 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.001F^2]$
$(\Delta/\sigma)_{\max} = 0.19$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}
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)

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

	x	y	z	$U_{\rm eq}$
Cl(1)	0.82907 (11)	0.36910 (5)	0.4589 (1)	0.087
O(1)	0.6928 (2)	0.1599 (1)	0.0285 (2)	0.056
C(2)	0.6982 (3)	0.1048 (2)	0.1119 (3)	0.048
C(3)	0.7107 (2)	0.1245 (1)	0.2700 (3)	0.037
C(4)	0.7316 (2)	0.1974 (1)	0.2646 (3)	0.037
C(5)	0.7644 (2)	0.2459 (1)	0.3702 (3)	0.042
C(6)	0.7839 (3)	0.3082 (2)	0.3268 (4)	0.053
C(7)	0.7700 (3)	0.3236 (2)	0.1824 (2)	0.062
C(8)	0.7365 (3)	0.2754 (2)	0.0761 (4)	0.058
C(9)	0.7187 (3)	0.2139 (2)	0.1209 (3)	0.044
O(10)	0.6929 (2)	0.0517 (1)	0.0603 (3)	0.067
C(11)	0.5979 (3)	0.1073 (2)	0.3008 (3)	0.044
C(12)	0.5398 (3)	0.0490 (2)	0.2526 (4)	0.066
C(13)	0.4398 (4)	0.0349 (3)	0.2847 (5)	0.082
C(14)	0.3970 (4)	0.0774 (3)	0.3655 (5)	0.084
C(15)	0.4512 (3)	0.1353 (2)	0.4090 (5)	0.076
C(16)	0.5503 (3)	0.1509 (2)	0.3769 (4)	0.057
Cl(1′)	1.12502 (8)	0.21490 (6)	0.1666 (1)	0.081
O(1′)	0.8920 (2)	−0.0121 (1)	0.3085 (3)	0.063
C(2′)	0.8153 (3)	0.0145 (2)	0.3697 (3)	0.051
C(3′)	0.8259 (2)	0.0897 (1)	0.3760 (3)	0.038
C(4′)	0.9229 (2)	0.0996 (2)	0.3105 (3)	0.043
C(5′)	0.9764 (3)	0.1546 (2)	0.2792 (3)	0.047
C(6′)	1.0581 (3)	0.1458 (2)	0.2076 (3)	0.057
C(7′)	1.0855 (3)	0.0848 (2)	0.1673 (4)	0.070
C(8′)	1.0329 (3)	0.0294 (2)	0.1990 (4)	0.070
C(9′)	0.9528 (3)	0.0385 (2)	0.2705 (3)	0.052
O(10′)	0.7549 (2)	−0.0202 (1)	0.4144 (3)	0.067
C(11′)	0.8496 (2)	0.1115 (1)	0.5348 (3)	0.038
C(12′)	0.7726 (3)	0.0966 (2)	0.6099 (3)	0.044
C(13′)	0.7891 (3)	0.1199 (2)	0.7492 (3)	0.054
C(14′)	0.8841 (3)	0.1571 (2)	0.8180 (4)	0.060
C(15′)	0.9635 (3)	0.1689 (2)	0.7474 (4)	0.062
C(16′)	0.9471 (3)	0.1466 (2)	0.6080 (4)	0.048

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

O(1)—C(2)	1.371 (4)	O(1′)—C(2′)	1.368 (5)
O(1)—C(9)	1.389 (4)	O(1′)—C(9′)	1.389 (4)
C(2)—C(3)	1.536 (5)	C(2′)—C(3′)	1.541 (5)
C(2)—O(10)	1.187 (4)	C(2′)—O(10′)	1.197 (5)
C(3)—C(4)	1.516 (4)	C(3′)—C(4′)	1.524 (4)
C(3)—C(11)	1.542 (4)	C(3′)—C(11′)	1.531 (4)
C(3)—C(3′)	1.624 (4)		
C(4)—C(5)	1.385 (4)	C(4′)—C(5′)	1.379 (5)
C(4)—C(9)	1.385 (4)	C(4′)—C(9′)	1.389 (5)
C(5)—C(6)	1.382 (5)	C(5′)—C(6′)	1.394 (5)
C(6)—C(7)	1.383 (6)	C(6′)—C(7′)	1.376 (6)
C(6)—Cl(1)	1.742 (4)	C(6′)—Cl(1′)	1.739 (4)
C(7)—C(8)	1.387 (6)	C(7′)—C(8′)	1.383 (7)
C(8)—C(9)	1.367 (5)	C(8′)—C(9′)	1.376 (6)
C(2)—O(1)—C(9)	108.4 (3)	C(2′)—O(1′)—C(9′)	108.4 (3)
O(1)—C(2)—C(3)	109.8 (3)	O(1′)—C(2′)—C(3′)	110.6 (3)
O(1)—C(2)—O(10)	121.2 (3)	O(1′)—C(2′)—O(10′)	120.3 (3)
C(3)—C(2)—O(10)	129.0 (3)	C(3′)—C(2′)—O(10′)	129.0 (3)
C(2)—C(3)—C(4)	100.9 (2)	C(2′)—C(3′)—C(4′)	100.5 (2)
C(2)—C(3)—C(11)	108.3 (2)	C(2′)—C(3′)—C(11′)	108.4 (2)
C(2)—C(3)—C(3′)	107.9 (2)	C(3)—C(3′)—C(2′)	111.4 (2)
C(4)—C(3)—C(11)	113.6 (2)	C(4′)—C(3′)—C(11′)	116.5 (2)
C(4)—C(3)—C(3′)	109.2 (2)	C(3)—C(3′)—C(4′)	108.5 (2)
C(11)—C(3)—C(3′)	115.7 (2)	C(3)—C(3′)—C(11′)	110.9 (2)
C(3)—C(4)—C(5)	133.7 (2)	C(3′)—C(4′)—C(5′)	133.2 (3)
C(3)—C(4)—C(9)	107.7 (2)	C(3′)—C(4′)—C(9′)	107.7 (3)
C(5)—C(4)—C(9)	118.5 (3)	C(5′)—C(4′)—C(9′)	119.0 (3)
O(1)—C(9)—C(4)	112.3 (3)	O(1′)—C(9′)—C(4′)	112.7 (3)
O(1)—C(9)—C(8)	123.6 (3)	O(1′)—C(9′)—C(8′)	123.8 (3)
C(4)—C(9)—C(8)	123.9 (3)	C(4′)—C(9′)—C(8′)	123.5 (3)

Program used for direct-methods structure determination: *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Program used for structure refinement: *SHELX*76 (Sheldrick, 1976). The H atoms were located from difference maps.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including bond distances and angles involving H atoms, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71832 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1055]

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threo-3-Fluoro-2-hydroxy-1,3-diphenyl-1-propanone and (1*RS*,2*RS*,3*RS*)-3-Fluoro-1,3-diphenyl-1,2-propanediol

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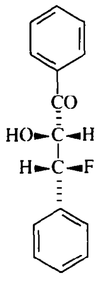
Abstract

The steric assignment of *threo*-3-fluoro-2-hydroxy-1,3-diphenyl-1-propanone, $C_{15}H_{13}FO_2$, has been confirmed. Reduction of this compound with sodium tetrahydridoborate gave a crystalline product identified as (1*RS*,2*RS*,3*RS*)-3-fluoro-1,3-diphenyl-1,2-propanediol, $C_{15}H_{15}FO_2$.

Comment

1,2-Diaryl-1,3-propanediols can be synthesized starting from 1,3-diaryl-2,3-epoxy-1-propanones. Treatment of such epoxides with boron trifluoride causes a rearrangement leading to 3-oxopropanals (or their difluoroboron complexes) (House & Ryerson, 1961; Li, Lundquist & Stomberg, 1993) and subsequent reduction yields the desired 1,2-diaryl-1,3-propanediols (Kristersson & Lundquist, 1980; Ahvonen, Brunow, Kristersson & Lundquist, 1983; Ralph, Ede, Robinson & Main, 1987; Tanaka, Hiroo, Ichino & Ito, 1989; Li, Lundquist & Stomberg, 1993). In some instances the boron trifluoride treatment leads to formation of fluorohydrins as by-products. Thus 2,3-epoxy-1,3-diphenyl-1-propanone gives substantial amounts of *threo*-3-fluoro-2-hydroxy-1,3-diphenyl-1-propanone (1) on treatment with about equimolar amounts of boron trifluoride in ether (House, 1956*a*; House & Ryerson, 1961).



(1)

The steric assignment of fluorohydrin (1) was derived from comparisons with the analogous *threo*-chlorohydrin (House, 1956*b*). The crystal structure determination described in this paper confirms that (1) has the *threo* configuration.

In two recent investigations (Ralph, Ede, Robinson & Main, 1987; Tanaka, Hiroo, Ichino & Ito, 1989) fluorohydrin formation on treatment of 1,3-diaryl-2,3-epoxy-1-propanones with boron trifluoride is reflected in the presence of 1,3-diaryl-3-fluoro-1,2-propanediols (together with 1,2-diaryl-1,3-propanediols) in the reaction mixtures resulting from reduction of the rearrangement products with tetrahydridoborate. Reduction of (1) with sodium tetrahydridoborate gave such a fluoro-substituted reduction product, namely (1*RS*,2*RS*,3*RS*)-3-fluoro-1,3-diphenyl-1,2-propanediol (2) (Li, Lundquist & Stomberg, 1993). The product was crystallized from benzene (m.p. 374–375 K). Its stereochemistry was elucidated by the crystal structure analysis presented in this paper. ^{1}H NMR examination of the mother liquor revealed the presence of small amounts of a stereoisomer of (2), the structure of which is proposed to be (1*RS*,2*SR*,3*SR*)-3-