Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

2,2′-[(Diphenylsilylene)dioxy]bis(5-chlorobenzophenone)

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.002 Å
R factor = 0.040
wR factor = 0.108
Data-to-parameter ratio = 22.7

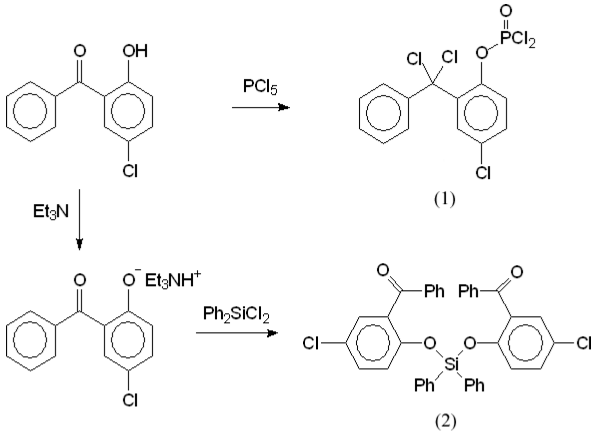
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 19 May 2004
Accepted 21 May 2004
Online 29 May 2004

The title compound, $C_{38}H_{26}Cl_2O_4Si$, was obtained from the tertiary-amine-catalyzed reaction of diphenyldichlorosilane with two equivalents of 5-chloro-2-hydroxybenzophenone. As expected, the silicon atom has a distorted tetrahedral environment.

Comment

In contrast with reactions of 2-hydroxybenzophenones with phosphorus pentachloride, which yielded unusual tetrachlorinated products such as (1) after loss of HCl (Pinkus & Meng, 1966), crystalline 1:1 or 2:1 products could not be isolated from analogous reactions with silicon tetrachloride (Pinkus & Ku, 1969). However, 2-hydroxybenzophenones reacted with diphenyldichlorosilane to form a crystalline product (2). This reaction product, a disubstituted diphenylsilene, is made by the nucleophillic action of a deprotonated hydroxybenzophenone on diphenyldichlorosilane as shown in the Scheme. The observation that a monosubstituted product cannot be isolated relates to the reactivity of such a species as an intermediate en route to the fully dechlorinated product. The electrophilicity of the Si atom is greatly enhanced by this first addition due to the highly electron-withdrawing character of the chlorinated benzophenone. The silicon-shielding effects of the first substituent's steric bulk is thus outweighed to the point that each successive equivalent of deprotonated hydroxybenzophenone attacks the monosubstituted product in preference to a separate molecule of dichlorodiphenylsilane. In this manner, only the disubstituted product is formed.



The molecular structure of (2) is shown in Fig. 1 and selected geometric parameters are presented in Table 1. The silicon environment is, as expected, a distorted tetrahedron. The nature of the distortion, however, is not as expected. The

DOI: 10.1107/S1600536804012516

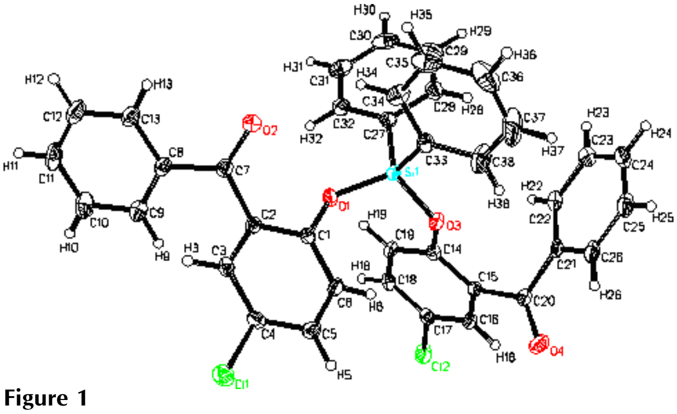


Figure 1
A view of the molecular structure of (2), with displacement ellipsoids drawn at the 50% probability level.

O1—Si—O3 and C27—Si—C33 angles are nearly standard at 110.25 (5) and 110.20 (6)°, respectively. The O3—Si—C27 angle is also only slightly increased, at 111.54 (6)°, while the O3—Si—C33 angle is contracted to 104.92 (5)°. This expansion/contraction is also seen in the O1—Si—C33 and O1—Si—C27 angles [115.46 (6) and 104.62 (5)°, respectively]. The distribution of angles, as well as the arrangement of the immediate substituents, about the central Si atom, is consistent with a C_2 axis bisecting the O1—Si—O3/C27—Si—C33 angles. This rotation axis is effectively maintained as far as the carbonyl groups, where differences in positioning of the terminal phenyl rings break the symmetry. All other bonds lengths and angles in the structure are within expected ranges.

Experimental

Diffraction-quality crystals of (2) were obtained by cooling a saturated solution of (2) in cyclohexane. Compound (2) was synthesized as previously reported in Pinkus & Ku (1969).

Crystal data

$C_{38}H_{26}Cl_2O_4Si$
$M_r = 645.58$
Triclinic, $P\bar{1}$
$a = 9.1403$ (8) Å
$b = 12.5346$ (10) Å
$c = 14.8510$ (13) Å
$\alpha = 109.503$ (3)°
$\beta = 104.308$ (4)°
$\gamma = 93.099$ (4)°
$V = 1536.6$ (2) Å^3

$Z = 2$
$D_x = 1.395$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5763 reflections
$\theta = 2.4$–30.4°
$\mu = 0.29$ mm^{-1}
$T = 273$ (2) K
Block, colorless
0.21 × 0.20 × 0.17 mm

Data collection

Bruker X8 APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.941$, $T_{\max} = 0.952$
24 157 measured reflections

9231 independent reflections
6876 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 30.5°$
$h = -13 \rightarrow 13$
$k = -17 \rightarrow 15$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.108$
$S = 1.09$
9231 reflections
406 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Table 1
Selected bond angles (°).

O1—Si1—O3	110.25 (5)	O1—Si1—C27	104.62 (5)
O1—Si1—C33	115.46 (6)	O3—Si1—C27	111.54 (5)
O3—Si1—C33	104.92 (5)	C33—Si1—C27	110.20 (6)

H atoms were included in calculated positions (C—H = 0.930 Å) and refined as riding atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm iso}$(parent C atom).

Data collection: *APEX*2 (Bruker, 2003); cell refinement: *APEX*2; data reduction: *SAINT-Plus* (Bruker, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

The Bruker X8 APEX diffractometer was purchased with funds received from the National Science Foundation Major Research Instrumentation Program Grant CHE-0321214. KK thanks the Robert A. Welch Foundation for support (AA-1508). AGP thanks the Public Health Service, National Institute of Health for support of a research grant.

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