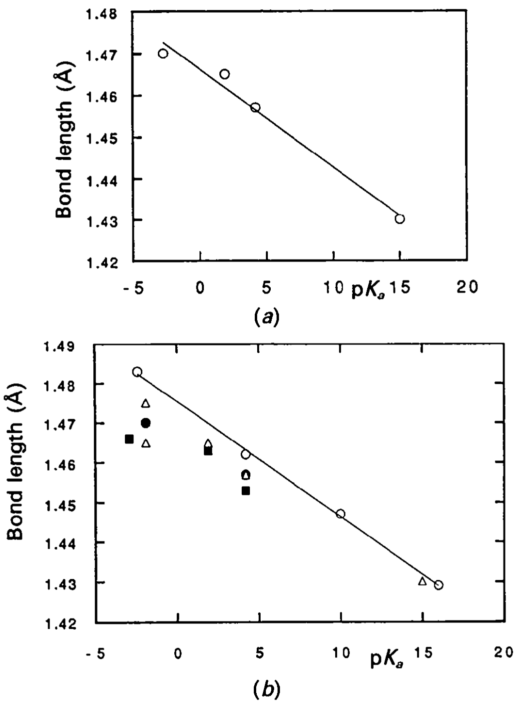


Fig. 2. (a) Plot of the C—O*X* bond length for compounds (1), with F and O*X* *trans* diaxial, *vs* the pK_a of the conjugate acid (HO*X*) of the leaving group. Data for compounds (1)–(3) of the previous paper (Jones, Kirby & Parker, 1992*a*), and for the two mesylates (2) and (3) (mean value, see text). The (least-squares) line drawn fits the equation:

$$\text{Bond length (Å)} = 1.466 - 2.35 \times 10^{-3}\text{p}K_a,$$

with a correlation coefficient, $r = 0.990$. (*b*) Plot of C—O*X* bond length for derivatives R_2CHO*X* of cyclohexanol *vs* the pK_a of the conjugate acid (HO*X*) of the leaving group. Open circles represent data for unsubstituted compounds. Other symbols represent the same parameter for derivatives of 2-fluorocyclohexanol; open triangles for diaxial compounds (data from this and the previous paper): filled symbols for equatorial O*X* (data from Jones, Kirby & Parker, 1992*b*,*d*). The F atom is either axial (circles) or equatorial (squares), and thus *gauche* to C—O*X*.

HO*X*, of the leaving group gives a good straight line (Fig. 2*a*). Both the intercept and the slope of this correlation are significantly smaller than those found for equatorial derivatives of cyclohexanol (Jones, Kirby & Parker, 1992*c*). The comparison of these correlations is a more reliable guide than comparing individual structures: Fig. 2(*b*) shows all our data, plotted as for Fig. 2(*a*), for nine axial and equatorial 2-fluorocyclohexanol derivatives, taken from this and the previous three papers, compared with bond-length data for the same range of derivatives of the non-fluorinated parent systems. Clearly the effect of β-fluorine, though generally small, is real and, furthermore, it is independent of geometry, as suggested in the previous paper (Jones, Kirby & Parker, 1992*a*). These effects will be discussed in a more general context elsewhere (Amos, Handy, Jones, Kirby, Parker, Percy & Su, 1992).

We thank the Fonds der Chemischen Industrie for support. The crystallographic work on (2) was carried out in Göttingen, at the Institut für Anorganische Chemie der Universität.

References

Amos, R. D., Handy, N. C., Jones, P. G., Kirby, A. J., Parker, J. K., Percy, J. M. & Su, M. D. (1992). *J. Chem. Soc. Perkin Trans.* 2. In the press.
Jones, P. G. & Kirby, A. J. (1979). *J. Chem. Soc. Chem. Commun.* pp. 288–289.
Jones, P. G. & Kirby, A. J. (1984). *J. Am. Chem. Soc.* **106**, 6207.
Jones, P. G., Kirby, A. J. & Parker, J. K. (1992*a*). *Acta Cryst.* C**48**, 859–864.
Jones, P. G., Kirby, A. J. & Parker, J. K. (1992*b*). *Acta Cryst.* C**48**, 855–858.
Jones, P. G., Kirby, A. J. & Parker, J. K. (1992*c*). *Acta Cryst.* C**48**, 849–851.
Jones, P. G., Kirby, A. J. & Parker, J. K. (1992*d*). *Acta Cryst.* C**48**, 852–855.
Sheldrick, G. M. (1990). *SHELXTL Users Manual.* Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1992). C**48**, 866–868

Bond Length and Reactivity. The Effect of β-Silicon. Structure of the 4-Phenylbenzoate Ester of 2-Trimethylsilylethanol

By Michael J. Doyle, Anthony J. Kirby, Jonathan M. Percy and Paul R. Raithby

University Chemical Laboratory, Cambridge CB2 1EW, England

(*Received* 14 *January* 1991; *accepted* 14 *October* 1991)

Abstract. 2-Trimethylsilylethyl 4-phenylbenzoate, $C_{18}H_{22}O_2Si$, $M_r = 299.47$, monoclinic, $P2_1/c$, $a = 6.256\,(1)$, $b = 16.608\,(3)$, $c = 17.012\,(4)$ Å, $\beta = 94.49\,(2)°$, $V = 1762.12$ Å^3, $Z = 4$, $D_x = 1.129$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 1.17$ mm^{-1}, $F(000) = 640$, $T = 293$ K. Final $R =$

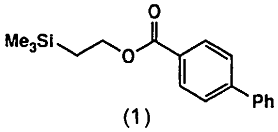
0108-2701/92/050866-03$06.00

0.053 for 2177 observed reflections [$F > 4\sigma(F)$] and 193 parameters. The molecule adopts the expected extended conformation, with the C—Si and C—O ester bonds antiperiplanar. The C—O*X* bond is slightly longer [1.466 (3) Å] than found for comparable alkyl ester bonds at primary centres, consistent with the expected $\sigma_{\mathrm{C-Si}}-\sigma^*_{\mathrm{C-O}}$ interaction in the ground state.

Introduction. We have suggested two rules which relate the length of a bond to the rate at which it is broken in ionic reactions in solution (Edwards, Jones & Kirby, 1986): (1) the longer the bond in a given system, the faster it breaks; and (2) the more reactive the system, the more sensitive is the length of the bond to structural variation. Our data refer specifically to C—O*X* bonds, but the principles should have broader application.

The basis of these effects is a contribution to the ground-state structure of systems *R*—O*X* from the valence bond tautomeric form $R^+\ {}^-\mathrm{O}X$, which is greater the more stable is either of the two ions involved. In this and the following paper we begin to examine the effect on the length of the *R*—O*X* bond of the introduction of Si. Silicon in the β-position is well known for its ability to stabilize carbocations (Fleming, 1979), and stands in contrast with the strongly electronegative F atom, discussed earlier in this series of papers.

We report here the structure of the 4-phenylbenzoate ester (1) of 2-trimethylsilylethanol. We had considerable difficulty in finding useful crystalline derivatives of β-silylated alcohols: of ten likely derivatives of 2-trimethylsilylethanol, for example, five were solids. Of these, three gave crystals which looked promising, but only one ester (1) diffracted well. Similarly, of six derivatives of 2-(*tert*-butyldimethylsilyl)ethanol, none gave useful crystals. So we have determined crystal structures for only two compounds.



(1)

Experimental. 2-Trimethylsilylethyl 4-phenylbenzoate (1) was prepared by the general method described previously (Jones, Kirby & Parker, 1992). Recrystallization from aqueous methanol gave crystals, m.p. 325.3–327 K. Single crystals were grown by vapour diffusion of water into a solution in *n*-butanol. Crystal: 0.30 × 0.38 × 0.50 mm; Nicolet *R*3*m*μ diffractometer, graphite-monochromated Cu $K\alpha$ radiation; cell parameters refined from diffractometer angles for 25 centred reflections ($45 < 2\theta < 55°$). Intensity data collected by θ–2θ scans for 3029 reflections with $5 < 2\theta < 120°$ (h 0–8, k 0–19, l −20–20); three standard reflections measured every 100 reflections showed no crystal decay; absorption correction based on an ellipsoid model and 304 azimuthal scan data from six independent reflections; max. and min. transmission factors 0.645 and 0.437, $\mu R = 0.23$; 2177 unique reflections (R_{int} 0.010) with $F > 4\sigma(F)$ were used in the analysis. Structure solved by direct methods and subsequent Fourier difference syntheses. Blocked-cascade least-squares refinement on *F*, anisotropic thermal parameters for all non-hydrogen atoms. H atoms were placed in idealized positions and allowed to ride on the relevant C atom, C—H 0.96 Å; each type of H was assigned a common isotropic thermal parameter. 193 parameters, $R = 0.053$, $wR = 0.075$, $w^{-1} = \sigma^2(F) + 0.00126F_o^2$, $S = 1.631$, $\Delta/\sigma = 0.014$ (mean) and 0.053 (max.), $\Delta\rho$ variations within 0.20 and -0.22 e Å^{-3}. The structure was solved and refined using *SHELXTL-Plus* (Sheldrick, 1990). Neutral-atom scattering factors are taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic coordinates for (1) are given in Table 1,* and derived parameters in Table 2. Fig. 1 shows a plot of (1), with the atom-numbering scheme.

The ester (1) crystallizes in the expected extended conformation, with the C—Si and C—O ester bonds antiperiplanar [dihedral angle 178.1 (2)°]. Other conformational parameters are unexceptional: the conformation about the Si—$\mathrm{CH_2}$ bond is staggered, the ester group is close to planar, and the dihedral angle between the two benzenoid rings of the biphenyl unit is 19.9 (5)°. The bond length of special interest, C(14)—O(2), is 1.466 (3) Å. As usual one must be careful not to draw more than provisional conclusions on the basis of a single structure, but this appears to be significantly longer than expected for a C—O ester bond. Two literature values, based on compounds in the Cambridge Structural Database, are available for the length of an alkyl ester bond at a primary centre. Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987) give 1.452 (9) Å for all esters of this type, while Allen & Kirby (1984) found the same value [1.452 (2) Å] for esters with only C—H or C—C bonds β to the C—O ester linkage.

The steric effect of the trimethylsilyl group ensures that trimethylsilylethyl derivatives will prefer the extended conformation, so for systems with dihedral

---

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54762 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0062]

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}*
C(1)	2252 (5)	2682 (2)	−2389 (2)	90 (1)
C(2)	1473 (7)	2427 (2)	−3126 (2)	111 (1)
C(3)	−440 (6)	2702 (2)	−3461 (2)	98 (1)
C(4)	−1586 (5)	3240 (2)	−3061 (2)	87 (1)
C(5)	−824 (4)	3501 (2)	−2317 (2)	73 (1)
C(6)	1112 (4)	3221 (1)	−1960 (1)	60 (1)
C(7)	1931 (4)	3489 (1)	−1162 (1)	55 (1)
C(8)	602 (4)	3823 (2)	−642 (1)	77 (1)
C(9)	1357 (4)	4090 (2)	95 (2)	78 (1)
C(10)	3499 (4)	4036 (1)	338 (1)	56 (1)
C(11)	4849 (4)	3690 (2)	−165 (2)	82 (1)
C(12)	4064 (4)	3427 (2)	−900 (2)	82 (1)
C(13)	4283 (4)	4369 (1)	1122 (1)	61 (1)
C(14)	7310 (5)	4528 (2)	2048 (1)	77 (1)
C(15)	6892 (4)	3979 (2)	2722 (1)	65 (1)
C(16)	11114 (5)	4404 (2)	3644 (2)	101 (1)
C(17)	7521 (6)	3596 (2)	4463 (2)	108 (1)
C(18)	7068 (6)	5330 (2)	3930 (2)	95 (1)
O(1)	3166 (3)	4727 (1)	1545 (1)	82 (1)
O(2)	6357 (3)	4220 (1)	1293 (1)	75 (1)
Si(1)	8163 (1)	4333 (1)	3697 (1)	66 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

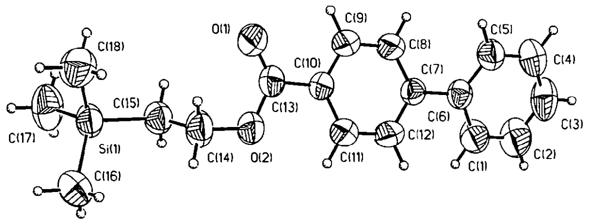


Fig. 1. The molecular structure of (1), showing the atomic labelling. The thermal ellipsoids are at the 50% probability level.

angles Si—C—C—OX other than 180° we needed to prepare derivatives of fixed conformation. One is described in the following paper.

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)—C(2)	1.375 (4)	C(1)—C(6)	1.388 (4)
C(2)—C(3)	1.364 (5)	C(3)—C(4)	1.361 (5)
C(4)—C(5)	1.386 (4)	C(5)—C(6)	1.391 (4)
C(6)—C(7)	1.482 (3)	C(7)—C(8)	1.377 (4)
C(7)—C(12)	1.377 (4)	C(8)—C(9)	1.377 (4)
C(9)—C(10)	1.374 (4)	C(10)—C(11)	1.374 (4)
C(10)—C(13)	1.491 (3)	C(11)—C(12)	1.379 (4)
C(13)—O(1)	1.200 (3)	C(13)—O(2)	1.331 (3)
C(14)—C(15)	1.503 (4)	C(14)—O(2)	1.466 (3)
C(15)—Si(1)	1.876 (2)	C(16)—Si(1)	1.859 (3)
C(17)—Si(1)	1.855 (4)	C(18)—Si(1)	1.847 (3)

C(2)—C(1)—C(6)	121.2 (3)	C(1)—C(2)—C(3)	121.0 (3)
C(2)—C(3)—C(4)	119.3 (3)	C(3)—C(4)—C(5)	120.3 (3)
C(4)—C(5)—C(6)	121.4 (3)	C(1)—C(6)—C(5)	116.8 (2)
C(1)—C(6)—C(7)	121.4 (2)	C(5)—C(6)—C(7)	121.8 (2)
C(6)—C(7)—C(8)	121.8 (2)	C(6)—C(7)—C(12)	122.1 (2)
C(8)—C(7)—C(12)	116.2 (2)	C(7)—C(8)—C(9)	122.2 (2)
C(8)—C(9)—C(10)	120.7 (2)	C(9)—C(10)—C(11)	118.2 (2)
C(9)—C(10)—C(13)	119.4 (2)	C(11)—C(10)—C(13)	122.4 (2)
C(10)—C(11)—C(12)	120.3 (2)	C(7)—C(12)—C(11)	122.5 (3)
C(10)—C(13)—O(1)	123.7 (2)	C(10)—C(13)—O(2)	111.9 (2)
O(1)—C(13)—O(2)	124.4 (2)	C(15)—C(14)—O(2)	112.0 (2)
C(14)—C(15)—Si(1)	113.4 (2)	C(13)—O(2)—C(14)	116.7 (2)
C(15)—Si(1)—C(16)	109.3 (1)	C(15)—Si(1)—C(17)	108.3 (1)
C(16)—Si(1)—C(17)	110.3 (2)	C(15)—Si(1)—C(18)	109.4 (1)
C(16)—Si(1)—C(18)	109.8 (2)	C(17)—Si(1)—C(18)	109.7 (2)

References

ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans* 2, pp. S1–S19.

ALLEN, F. H. & KIRBY, A. J. (1984). *J. Am. Chem. Soc.* **106**, 6197–6200.

EDWARDS, M. R., JONES, P. G. & KIRBY, A. J. (1986). *J. Am. Chem. Soc.* **108**, 7067–7072.

FLEMING, I. (1979). *Comprehensive Organic Chemistry*, Vol. 3, edited by D. H. R. BARTON & W. D. OLLIS, pp. 541–686. Oxford: Pergamon Press.

JONES, P. G., KIRBY, A. J. & PARKER, J. K. (1992). *Acta Cryst.* C**48**, 844–847.

SHELDRICK, G. M. (1990). *SHELXTL Users Manual*. Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1992). C**48**, 868–871

Bond Length and Reactivity. The Effect of β-Silicon. Structure of the 3,5-Dinitrobenzoate Ester of *trans*-2-(Dimethylphenylsilyl)cyclohexanol

BY PETER G. JONES

Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, 3300 *Braunschweig, Germany*

AND ANTHONY J. KIRBY AND JANE K. PARKER

*University Chemical Laboratory, Cambridge CB*2 1*EW, England*

(*Received* 14 *January* 1991; *accepted* 14 *October* 1991)

Abstract. *trans*-2-(Dimethylphenylsilyl)cyclohexyl 3,5-dinitrobenzoate, $C_{21}H_{24}N_2O_6Si$, $M_r = 428.52$, triclinic, $P\overline{1}$, $a = 7.9566\ (14)$, $b = 13.110\ (3)$, $c = 20.844\ (5)$ Å, $\alpha = 96.32\ (2)$, $\beta = 90.73\ (2)$, $\gamma = 90.24\ (2)$°, $V = 2161$ Å^3, $Z = 4$, $D_x = 1.317$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.14$ mm^{-1}, $F(000) =$

0108-2701/92/050868-04$06.00