

Table 2. Selected geometric parameters (Å, °)

C1—S1	1.747 (3)	C8—C9	1.369 (5)
C2—C3	1.377 (4)	C8—O5	1.400 (4)
C2—C7	1.396 (4)	C9—C10	1.376 (5)
C2—N1	1.409 (4)	C10—C11	1.360 (5)
C3—C4	1.387 (4)	C11—C12	1.364 (5)
C4—C5	1.364 (4)	C12—C13	1.362 (5)
C5—C6	1.382 (4)	N1—S1	1.640 (2)
C5—N2	1.464 (4)	N2—O4	1.217 (4)
C6—C7	1.377 (4)	N2—O3	1.221 (3)
C7—O5	1.377 (3)	O1—S1	1.431 (2)
C8—C13	1.364 (5)	O2—S1	1.431 (2)
C3—C2—C7	119.1 (3)	C11—C10—C9	120.1 (3)
C3—C2—N1	124.3 (3)	C10—C11—C12	120.0 (3)
C7—C2—N1	116.6 (2)	C13—C12—C11	121.1 (4)
C2—C3—C4	120.6 (3)	C12—C13—C8	118.5 (3)
C5—C4—C3	118.6 (3)	C2—N1—S1	124.7 (2)
C4—C5—C6	123.1 (3)	O4—N2—O3	122.7 (3)
C4—C5—N2	119.3 (3)	O4—N2—C5	118.9 (3)
C6—C5—N2	117.6 (3)	O3—N2—C5	118.4 (3)
C7—C6—C5	117.4 (3)	C7—O5—C8	119.7 (2)
C6—C7—O5	124.8 (3)	O2—S1—O1	119.40 (14)
C6—C7—C2	121.3 (3)	O2—S1—N1	104.82 (12)
O5—C7—C2	113.8 (3)	O1—S1—N1	108.43 (13)
C13—C8—C9	121.6 (3)	O2—S1—C1	109.7 (2)
C13—C8—O5	117.6 (3)	O1—S1—C1	108.01 (14)
C9—C8—O5	120.5 (3)	N1—S1—C1	105.7 (2)
C8—C9—C10	118.7 (3)		
C7—C2—N1—S1	-155.6 (2)	C6—C7—O5—C8	6.2 (5)
C6—C5—N2—O4	-6.0 (4)	C13—C8—O5—C7	-111.4 (4)
C6—C5—N2—O3	171.9 (3)	C2—N1—S1—O2	175.1 (3)

Data collection: *DIF4* (Stoe & Cie, 1988a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1976). Software used to prepare material for publication: *SHELXL93*.

The authors thank M. M. Vermeire for his helpful assistance in the diffractometry measurements and the FNRS for financial support.

Lists of structure factors, anisotropic displacement parameters, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: PA1137). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 509–511

Methyl 3-[2-(*tert*-Butylthio)phenyl]propenoate

ALEXANDER J. BLAKE*

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

J. I. G. CADOGAN†

BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN, England

FOKKE J. J. DIJKSMA, ROBERT O. GOULD,
ANDREW D. MACPHERSON AND HAMISH McNAB

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

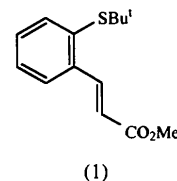
(Received 3 August 1994; accepted 23 August 1994)

Abstract

The effects of steric strain in methyl 3-[2-(*tert*-butylthio)phenyl]propenoate (C₁₄H₁₈O₂S) are seen in the distribution of C—C bond lengths within the phenyl ring and in the placement of the *tert*-butyl substituent.

Comment

The title compound, (1), represents a simple example of a sterically congested *ortho*-substituted cinnamate ester. *Ortho*-substitution does not appear to affect the bond lengths in the acrylate chain, which are very similar to those seen in remotely substituted cinnamates (Talberg, 1978; Nakanishi & Sasada, 1978). Similarly, the C—S bonds are only slightly different from their normal values (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). In contrast, the geometry of the benzene ring is substantially distorted, with the bond between the two substituted C atoms [C1—C2 1.409 (2) Å] somewhat longer than the other *ortho* bonds [C2—C3 1.398 (2), C1—C6 1.401 (2) Å]. These three bonds are significantly longer than the other three ring C—C distances [1.375 (2), 1.378 (3), 1.385 (3) Å].



† Present address: Department of Chemistry, Imperial College of Science, Technology & Medicine, South Kensington, London SW7 2AY, England.

Although the bond angles within the acrylate chain assume typical values (Talberg, 1978; Nakanishi & Sasada, 1978), the *exo* angles subtended at C1 are almost identical in (1): generally, the *transoid* angle C2—C1—C7 is larger than the *cisoid* angle C6—C1—C7 by up to 4°, although there are indications from the literature (Albertsson, Oskarsson & Svensson, 1978) that very minor structural changes at distant sites can affect these parameters. The relatively acute endocyclic angle at C1 is typical of those seen for acrylates (Talberg, 1978; Nakanishi & Sasada, 1978) and for electron-withdrawing substituents in general. The unequal *exo* angles at C2 may be attributed to steric repulsion. Remarkably, although two of the S—C—C angles within the *S-tert*-butyl group are very similar [110.76(11) and 111.05(11)°], the angle involving the staggered methyl group C3B is only 103.18(11)°; the C—C—C angles all lie *ca* 1° above the ideal tetrahedral value.

The acrylate chain adopts an all-*trans* configuration and the cinnamate unit overall has only minor deviations from planarity. The S atom lies 0.04 Å out of the plane of the benzene ring, in the direction of the *tert*-butyl group. The S-*tert*-butyl group is twisted by 86° from the plane of the benzene ring, a phenomenon also seen in an *S-tert*-alkyl thiophenol derivative without an *ortho* substituent, where a twist of 82° was observed (Kozikowski, Huie & Springer, 1982).

Experimental

The title compound was made by a Wittig reaction of 2-(*tert*-butylthio)benzaldehyde with methyl triphenylphosphoranylideneacetate in dichloromethane (MacPherson, 1994; Cadogan, MacPherson & McNab, 1994). Crystals were grown from hexane solution.

Crystal data

C₁₄H₁₈O₂S
M_r = 250.34
 Monoclinic
*P*2₁/*n*
a = 5.8813 (14) Å
b = 15.474 (3) Å
c = 14.919 (6) Å
 β = 95.64 (3)°
V = 1351.2 (7) Å³
Z = 4
D_x = 1.231 Mg m⁻³

Mo K α radiation
 λ = 0.71073 Å
 Cell parameters from 60 reflections
 θ = 10–16°
 μ = 0.228 mm⁻¹
T = 150.0 (2) K
 Block
 0.60 × 0.50 × 0.35 mm
 Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
 ω -2 θ scans of variable width using on-line profile-fitting (Clegg, 1981)
 Absorption correction: none
 3471 measured reflections
 2379 independent reflections
 2028 observed reflections [*I* > 2 σ (*I*)]

*R*_{int} = 0.0112
 θ _{max} = 25.06°
h = -7 → 6
k = -6 → 18
l = 0 → 17
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.0295
wR(*F*²) = 0.0727
S = 1.071
 2366 reflections
 154 parameters
 H atoms placed in calculated positions, with *U*_{iso} = 1.2*U*_{eq} of the C atom on which the H atom is riding

$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 0.5806P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.029$
 $\Delta\rho_{\max} = 0.181 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.258 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

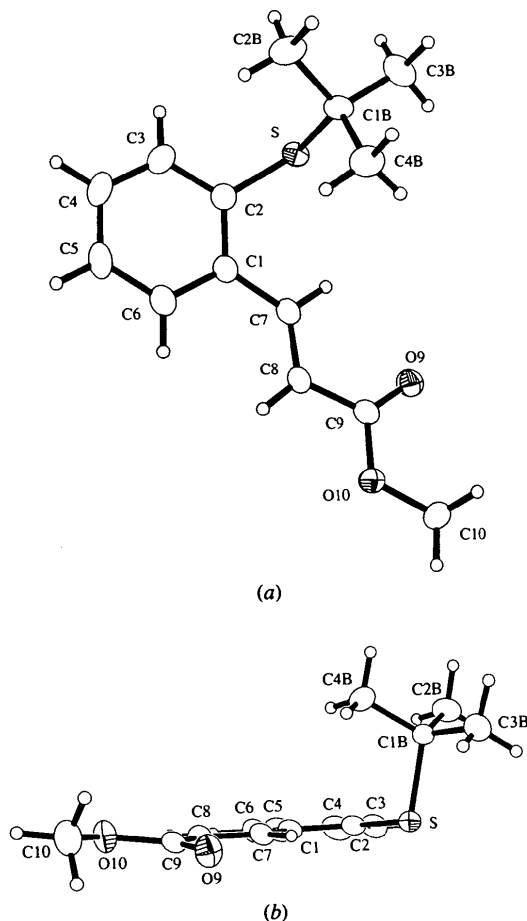


Fig. 1. (a) A view of the molecule with atom-numbering scheme and (b) an orthogonal view showing the orientation of the *S-tert*-butyl substituent. Displacement ellipsoids enclose 50% probability surfaces.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
C1	0.5699 (3)	0.53306 (10)	0.25586 (9)	0.0240 (3)
C2	0.3632 (3)	0.50441 (10)	0.20951 (9)	0.0247 (3)
C3	0.2175 (3)	0.56423 (11)	0.16317 (11)	0.0322 (4)
C4	0.2770 (3)	0.65017 (12)	0.15906 (11)	0.0379 (4)
C5	0.4836 (3)	0.67828 (11)	0.20171 (11)	0.0358 (4)
C6	0.6260 (3)	0.62073 (10)	0.24976 (11)	0.0303 (4)
C7	0.7185 (3)	0.47344 (10)	0.31084 (9)	0.0238 (3)
C8	0.9192 (3)	0.49057 (10)	0.35580 (10)	0.0241 (3)
C9	1.0447 (3)	0.42195 (10)	0.40793 (9)	0.0229 (3)
O9	0.9741 (2)	0.35037 (7)	0.42082 (7)	0.0308 (3)
O10	1.2549 (2)	0.44878 (7)	0.43987 (7)	0.0292 (3)
C10	1.3961 (3)	0.38478 (11)	0.48858 (12)	0.0339 (4)
S	0.27503 (6)	0.39442 (3)	0.21009 (2)	0.02445 (12)
C1B	0.3771 (2)	0.34955 (10)	0.10608 (10)	0.0252 (3)
C2B	0.2647 (3)	0.39574 (13)	0.02310 (11)	0.0376 (4)
C3B	0.2991 (3)	0.25586 (12)	0.10687 (12)	0.0384 (4)
C4B	0.6358 (3)	0.35467 (13)	0.10938 (12)	0.0357 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

C1—C2	1.409 (2)	C7—C8	1.326 (2)
C2—C3	1.398 (2)	C8—C9	1.471 (2)
C3—C4	1.378 (3)	C9—O9	1.205 (2)
C4—C5	1.385 (3)	C9—O10	1.346 (2)
C5—C6	1.375 (2)	O10—C10	1.442 (2)
C6—C1	1.401 (2)	C2—S	1.780 (2)
C1—C7	1.465 (2)	S—C1B	1.853 (2)
C6—C1—C2	118.04 (14)	O9—C9—O10	123.10 (14)
C3—C2—C1	119.46 (15)	O9—C9—C8	125.79 (14)
C4—C3—C2	121.0 (2)	O10—C9—C8	111.11 (13)
C3—C4—C5	119.9 (2)	C9—O10—C10	115.47 (12)
C6—C5—C4	119.9 (2)	C3—C2—S	118.09 (12)
C5—C6—C1	121.7 (2)	C1—C2—S	122.43 (12)
C6—C1—C7	120.96 (14)	C2—S—C1B	103.63 (7)
C2—C1—C7	120.98 (14)	C4B—C1B—S	111.05 (11)
C8—C7—C1	127.57 (15)	C3B—C1B—S	103.18 (11)
C7—C8—C9	119.91 (14)	C2B—C1B—S	110.76 (11)
C6—C1—C7—C8	-3.8 (2)	O9—C9—O10—C10	2.1 (2)
C2—C1—C7—C8	177.96 (15)	C8—C9—O10—C10	-177.26 (13)
C1—C7—C8—C9	179.88 (13)	C3—C2—S—C1B	87.08 (13)
C7—C8—C9—O9	-6.6 (2)	C1—C2—S—C1B	-94.72 (13)
C7—C8—C9—O10	172.76 (13)		

Data were acquired at 150 K by placing the crystal in the gas stream of an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986). Data collection: *DIF4* (Stoe & Cie, 1988a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXS90* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL92* (Sheldrick, 1992a). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992b).

We thank the SERC for provision of a four-circle diffractometer, British Petroleum PLC for a research studentship (to ADM), and the ERASMUS programme of the European Union for a studentship (to FJJD).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C51, 511–515

A Solvate of the Diacetate Salt of the Octaethyltetraphenylporphyrin Dication, $\text{H}_4\text{OETPP}^{2+} \cdot 2\text{CH}_3\text{COO}^- \cdot 3\text{CH}_3\text{COOH} \cdot \text{CH}_2\text{Cl}_2$

K. M. BARKIGIA AND J. FAJER

Department of Applied Science, Brookhaven National Laboratory, Upton, New York 11973, USA

M. D. BERBER AND K. M. SMITH

Department of Chemistry, University of California, Davis, California 95616, USA

(Received 3 March 1994; accepted 2 August 1994)

Abstract

The structure of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin(2+) diacetate acetic acid dichloromethane solvate, $\text{C}_{60}\text{H}_{64}\text{N}_4^{2+} \cdot 2\text{C}_2\text{H}_3\text{O}_2^- \cdot 3\text{C}_2\text{H}_4\text{O}_2 \cdot \text{CH}_2\text{Cl}_2$, has been determined at 200 K. The molecule is severely non-planar and adopts an S_4 saddle shape. It is the most distorted member of the OETPP series reported to date, with displacements of the β -pyrrole C atoms from the plane of the four N atoms as great as 1.42 Å and acute tilts of the phenyl rings relative to the porphyrin plane. The two acetate counterions act as bidentate ligands which bond to the H atoms on opposite pairs of N atoms. The crystal lattice also contains three acetic acid molecules of solvation