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Key indicators

Single-crystal X-ray study
 T = 187 K
 Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
 Disorder in main residue
 R factor = 0.048
 wR factor = 0.134
 Data-to-parameter ratio = 18.1

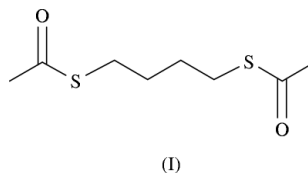
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Butanedithiol diacetate

In the solid state, molecules of butane-1,4-diyl bis(S-thioacetate), $\text{C}_8\text{H}_{14}\text{O}_2\text{S}_2$, are centrosymmetric and are associated *via* weak hydrogen bonds. The molecular structure, determined by X-ray crystallography, is in good agreement with that obtained by density functional geometry optimization.

Comment

Thioesters are very important acetylating agents in biochemical processes, as well as in many chemical transformations (Nicolaou, 1977; Hiram *et al.*, 1979; Zheng *et al.*, 1999). We obtained butanedithiol diacetate, $\text{H}_3\text{CC}(\text{O})\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SC}(\text{O})\text{CH}_3$, (I), as a by-product in the synthesis of 1,4-butanedithiol monoacetate, $\text{HSCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SC}(\text{O})\text{CH}_3$, (II), in a procedure similar to the preparation of ethanedithiol monoacetate and ethanedithiol diacetate (Wiesler *et al.*, 1996; Fleischer & Schollmeyer, 2001).



The molecular structure of (I), as found in the solid state, is depicted in Fig. 1; the molecule is centrosymmetric. Table 1 shows a comparison of selected structural parameters from the crystal structure with those obtained by a density functional (DF) geometry optimization. The molecular structure was first optimized at the Hartree–Fock level with a 6-31G(d) basis set, starting from the molecular structure as found in the solid state. Subsequently the structure was re-optimized employing density functional theory (DFT) and a larger basis set [B3LYP/6-311+G(2d,p)]. Apart from the two S–C and the C1–C1ⁱ distances [symmetry code: (i) 1 – x, 1 – y, 1 – z], the DF bond lengths and angles agree quite well with the experimental values. The torsion angles C1ⁱ–C1–C2–S3 and C1–C2–S3–C4 differ substantially between the solid state and the DF-calculated isolated molecule. We attribute the differences in the above-mentioned bond distances to the chosen level of theory, but the difference in torsion angles to intermolecular hydrogen bonds in the solid state [O5ⁱⁱ...C6 = 3.497 (3) Å and O5ⁱⁱ...H–C6 = 168.1 (2)°; symmetry code: (ii) x, ½ – y, ½ + z]. The structural parameters of (I) agree well with those found for other compounds containing an S-acetyl moiety (Fleischer & Schollmeyer, 2001; Evans *et al.*, 1999; Divjaković *et al.*, 1992; Mackay *et al.*, 1992; Huber *et al.*, 1984; Mattes & Waldmann, 1983; Mattes *et al.*, 1977; Kiel *et al.*,

Received 6 May 2003
 Accepted 12 May 2003
 Online 23 May 2003

1974). This implies that the *S*-acetyl fragment is a relatively rigid structural unit, a hypothesis supported by an analysis of the bonding situation in terms of natural bond orbitals (Fleischer & Schollmeyer, 2001).

Experimental

Butanedithiol diacetate, (I), was obtained as a by-product in the synthesis of 1,4-butanedithiol monoacetate, (II), in a procedure similar to the preparation of ethanedithiol monoacetate and ethanedithiol diacetate (Wiesler *et al.*, 1996; Fleischer & Schollmeyer, 2001). Crystals of (I) precipitated at 278 K from its solution in (II). They were washed with cold petroleum ether and identified by elemental analysis and ¹H NMR.

Crystal data

$C_8H_{14}O_2S_2$	$D_x = 1.310 \text{ Mg m}^{-3}$
$M_r = 206.31$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 6.1998 (7) \text{ \AA}$	$\theta = 57\text{--}73^\circ$
$b = 8.0292 (7) \text{ \AA}$	$\mu = 4.31 \text{ mm}^{-1}$
$c = 10.5650 (10) \text{ \AA}$	$T = 187 (2) \text{ K}$
$\beta = 95.942 (4)^\circ$	Block, colorless
$V = 523.09 (9) \text{ \AA}^3$	$0.25 \times 0.20 \times 0.15 \text{ mm}$
$Z = 2$	

Data collection

Enraf–Nonius CAD-4 diffractometer	908 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{\text{int}} = 0.169$
Absorption correction: ψ scan (CORINC; Dräger & Gattow, 1971)	$\theta_{\text{max}} = 73.8^\circ$
$T_{\text{min}} = 0.383$, $T_{\text{max}} = 0.524$	$h = -7 \rightarrow 7$
1126 measured reflections	$k = 0 \rightarrow 10$
1067 independent reflections	$l = 0 \rightarrow 13$
	3 standard reflections
	frequency: 60 min
	intensity decay: 5%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.048$	$w = 1/[\sigma^2(F_o^2) + (0.0915P)^2]$
$wR(F^2) = 0.134$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.12$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1067 reflections	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
59 parameters	$\Delta\rho_{\text{min}} = -0.84 \text{ e \AA}^{-3}$

Table 1

Comparison of selected structural parameters ($\text{\AA},^\circ$) from the molecular structure of (I) in the solid state (XRD) and from density functional (DF) geometry optimization [$B3LYP/6\text{-}311+G(2d,p)$] (Frisch *et al.*, 1995).

	XRD	DF
C1–C1 ⁱ	1.517 (4)	1.534
C1–C2	1.523 (3)	1.527
C2–S3	1.809 (2)	1.834
S3–C4	1.766 (3)	1.795
C4–C6	1.506 (3)	1.512
C4–O5	1.207 (3)	1.205
C1 ⁱ –C1–C2	113.3 (2)	111.6
C1–C2–S3	113.6 (2)	110.4
C2–S3–C4	101.0 (1)	100.1
S3–C4–C6	113.2 (2)	113.6
O5–C4–C6	123.7 (3)	123.5
O5–C4–S3	123.1 (2)	122.9
C1 ⁱ –C1–C2–S3	67.6 (3)	179.9
C1–C2–S3–C4	82.7 (2)	182.1
C2–S3–C4–O5	0.8 (2)	0.3
C2–S3–C4–C6	179.5 (2)	180.5

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

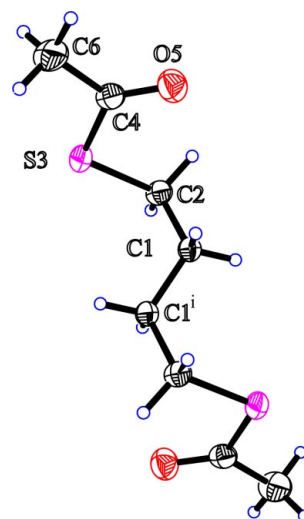


Figure 1

ORTEP (Johnson, 1976) view of the centrosymmetric molecule of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of fixed radius. The methyl group is disordered (0.52:0.48, ratio fixed) and only one set of H atoms bound to C6 is shown.

Chemically equivalent H atoms were placed at calculated positions and were refined isotropically with the same displacement parameters using riding motion. The two different groups of H atoms resulting from the disorder of the methyl group were treated with two independent displacement parameters.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL97*.

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