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Low-temperature 4-thiacyclohexyl *m*-nitrobenzoate

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The crystal structure of the title compound, $C_{12}H_{13}NO_4S$, reveals that the molecule exists with the ester group in the axial conformation, which differs from that observed in solution. The C—O bond distance from the cyclohexyl group to the ester O atom is 1.471 (2) Å. The structure was determined at 130 K.

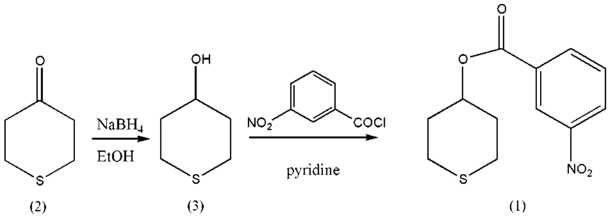
Key indicators

Single-crystal X-ray study
T = 130 K
Mean σ(C–C) = 0.003 Å
R factor = 0.047
wR factor = 0.132
Data-to-parameter ratio = 13.3

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

Comment

As part of our studies on the factors influencing C—O*R* (*R* = hydroxy, ester or ether) bond distances (White & Robertson, 1992; Green *et al.*, 2000; Pool *et al.*, 2000), we have determined the structure of 4-thiacyclohexyl *m*-nitrobenzoate, (1). C—O bond distances are sensitive to the effects of electron donation into the C—O antibonding orbital (Amos *et al.*, 1992). We were interested in establishing whether a through-bond interaction between the sulfur lone pair of electrons and the C—O bond in the ester (1) (Fig. 1) would result in any significant lengthening of the C—O(ester) bond.



However, the crystal structure of (1) (Fig. 2) reveals that this ester surprisingly exists in the solid state with the ester group in the axial conformation. This contrasts with the behaviour of (1) in solution, where ^{1}H NMR reveals that it exists in the equatorial conformation. Presumably optimization of the packing forces overcomes the natural preference for the ester to take up an equatorial site. Examination of the packing of (1) (Fig. 3) suggests that it is dominated by π–π stacking of the electron-deficient aromatic rings. The aromatic rings of the molecules of (1) (Fig. 4) stack across a crystallographic inversion centre with a spacing of 3.35 Å.

The C3—O1 bond distance in (1) is 1.474 (2) Å, showing good agreement with that predicted for an axial cyclohexyl *m*-nitrobenzoate ester (1.471 Å; Spiniello & White, 2003). This

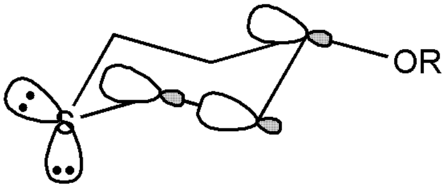


Figure 1
The proposed through-bond interaction between the sulfur lone pair and the C—O*R* antibonding orbital.

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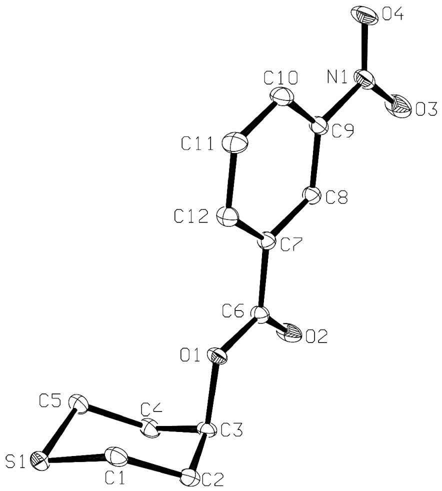

Figure 2
The molecular structure of (1), with displacement ellipsoids drawn at the 20% probability level. H atoms have been omitted for clarity.

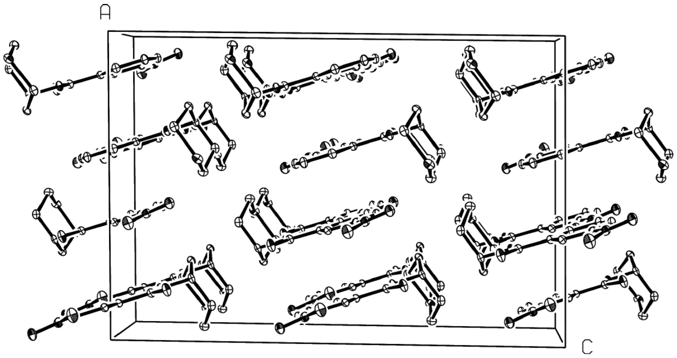

Figure 3
Crystal packing diagram of (1), with displacement ellipsoids drawn at the 20% probability level.

is based on the relationship between the C—O*R* bond distance and the pK_a value for *R*OH for axial cyclohexyl esters: C—O*R* (Å) = 1.480–2.77 × 10^{-3} × pK_a(*R*OH) and uses a value of *ca* 3.49 for the pK_a value for *m*-nitrobenzoic acid (Lide, 2000).

Experimental

The title compound, (1), was prepared in two steps from 4-thiacyclohexanone, (2), as outlined in the scheme. Thus, (2) was reduced to thiacyclohexan-4-ol, (3), using sodium borohydride in ethanol, and the secondary alcohol (3) was converted into the *m*-nitrobenzoate ester (1) by reaction with *m*-nitrobenzoyl chloride in pyridine, followed by aqueous work-up. Crystals of (1) were grown by slow evaporation of a pentane solution.

Crystal data

$C_{12}H_{13}NO_4S$
M_r = 267.29
Monoclinic, $C2/c$
a = 20.736 (4) Å
b = 8.4331 (17) Å
c = 14.106 (3) Å
β = 90.971 (3)°
V = 2466.3 (9) Å^3
Z = 8

D_x = 1.440 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2963 reflections
θ = 2.4–28.0°
μ = 0.27 mm^{-1}
T = 130 (2) K
Block, colourless
0.30 × 0.15 × 0.10 mm

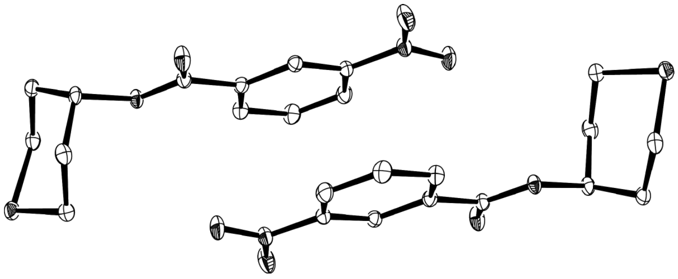

Figure 4
The π–π stacking within centrosymmetric pairs of (1).

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
6668 measured reflections
2173 independent reflections

1779 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.082
$\theta_{\rm max}$ = 25.0°
$h = -24 \rightarrow 24$
$k = -10 \rightarrow 4$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.132
S = 0.99
2173 reflections
163 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0869P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.48 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.528 (3)	C3—O1	1.474 (2)
C1—S1	1.808 (2)	C4—C5	1.514 (3)
C2—C3	1.513 (3)	C5—S1	1.815 (2)
C2—C1—S1	112.41 (15)	C2—C3—C4	113.97 (17)
C3—C2—C1	113.68 (17)	C5—C4—C3	113.47 (17)
O1—C3—C2	105.84 (15)	C4—C5—S1	112.93 (15)
O1—C3—C4	109.13 (15)		
S1—C1—C2—C3	59.4 (2)	O1—C3—C4—C5	−61.0 (2)
C1—C2—C3—O1	62.8 (2)	C2—C3—C4—C5	57.0 (2)
C1—C2—C3—C4	−57.2 (2)	C3—C4—C5—S1	−59.3 (2)

All H atoms were refined as riding in idealized positions, with displacement parameters fixed at 1.2 times $U_{\rm eq}$ of the parent atom. C—H distances were fixed ranging from 1.00 Å for methine down to 0.95 Å for aromatic.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

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