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Ethyl 2-[(1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)hydrazono]-2-(4-nitrophenylsulfanyl)acetate

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Key indicators

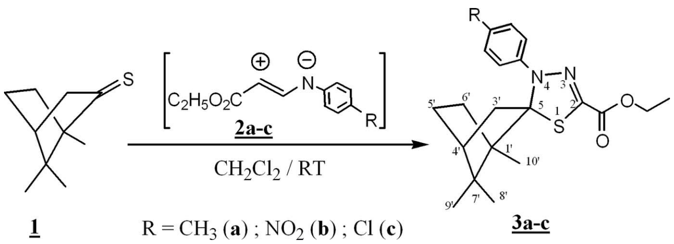
Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.009 Å
Disorder in main residue
R factor = 0.089
wR factor = 0.255
Data-to-parameter ratio = 13.3

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

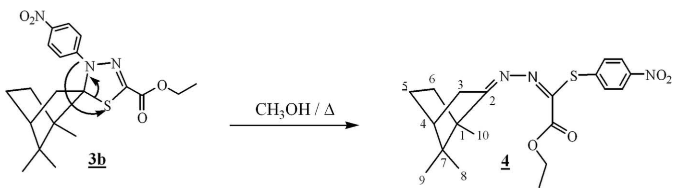
Heating ethyl 4,5-dihydro-4-(4-nitrophenyl)-spiro[1,3,4-thiadiazole-5,2′-camphane]-2-carboxylate in methanol provided the unusual rearrangement product (C_9H_{19})N_2C($SC_6H_4NO_2$)-($COOC_2H_5$) or $C_{20}H_{25}N_3O_4S$, whose structure was confirmed by an X-ray diffraction study. The structure features a camphor group connected through a hydrazine fragment to a nitrophenylsulfanyl group and an ethoxycarbonyl group.

Comment

In our search for new functionalized and heterocyclic systems from naturally occurring terpenes (Ziyat *et al.*, 2002, 2004; Fdil *et al.*, 2002; Feddouli, El Kadib *et al.*, 2004; Dakir *et al.*, 2004), we recently reported that (1*R*)-thiocamphor, (1), and *C*-ethoxycarbonylnitrilimines (2*a*)–(2*c*) react efficiently to give, diastereoselectively, the novel spiranic 1,3,4-thiadiazolines (3*a*)–(3*c*), whose structures and absolute configurations were proved beyond doubt using X-ray diffraction (Feddouli, Ait Itto *et al.*, 2004) (see first scheme below). We have also commented that some of the diazolo rings reported in the literature are unstable (Huisgen *et al.*, 2001). This prompted us to examine the thermal stability of our new spiranic 1,3,4-thiadiazolines (3*a*)–(3*c*).



Thus, thiadiazoline (3*b*) was heated under reflux in methanol for 12 h, to give a new compound, (4), in 50% yield (the reaction was monitored with thin-layer chromatography.). The EI mass spectrum of (4) exhibited the parent peak at *m*/*z* = 403 (15%) showing a molecular formula similar to that for (3*b*). The NMR characteristics of (3*b*) and (4) are also similar, with only a few differences in some ^{1}H and ^{13}C chemical shifts. The most pronounced difference is revealed by the ^{13}C NMR spectrum of (4), where we note the disappearance of the spiranic C signal and the appearance of a new Csp^2 resonance at 180.1 p.p.m. All these spectroscopic data are consistent with a rearrangement product but did not allow us to elucidate the exact structure of (4). Thus, an X-ray structural study was conducted to confirm, unambiguously, the rearrangement structure for (4).



The molecular structure of (4) (Fig. 1) is built up from a camphor group connected through a hydrazine fragment to a nitrophenylthio group and a carboxylic ethyl ester group. The formation of (4) could be explained by an opening of the heterocyclic nucleus with simultaneous migration of the aryl group to the S atom (see second scheme above). The geometry of the camphor and hydrazine groups agrees with those of related compounds (Shaw *et al.*, 1994, 1998). The nitrophenylthio group is planar and displays usual bond lengths and angles (Cambridge Structural Database, Version 5.26; Allen, 2002).

Experimental

Product (3*b*) (0.40 g, 0.99 mmol) in methanol (20 ml) was refluxed for 4 d. The solution was then concentrated under reduced pressure and the resulting residue was purified by chromatography (SiO_2, hexane/ethyl acetate 99:1) and recrystallized from pentane [yield 50%, m.p. 345–346 K (pentane)]; $[\alpha]_D^{25} = -8.86$ (c = 5, $CHCl_3$).

Crystal data

$C_{20}H_{25}N_3O_4S$
$M_r = 403.49$
Orthorhombic, $P2_12_12_1$
$a = 6.9124$ (14) Å
$b = 15.398$ (3) Å
$c = 19.778$ (4) Å
$V = 2105.2$ (7) Å^3
$Z = 4$
$D_x = 1.273$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2834 reflections
$\theta = 3.1$–31.0°
$\mu = 0.18$ mm^{-1}
$T = 180$ (2) K
Block, colorless
0.55 × 0.32 × 0.20 mm

Data collection

Oxford Diffraction XCALIBUR diffractometer
ω and φ scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.890$, $T_{\max} = 0.956$
14039 measured reflections

3710 independent reflections
2657 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.123$
$\theta_{\max} = 25.0°$
$h = -8 \rightarrow 7$
$k = -17 \rightarrow 18$
$l = -23 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.089$
$wR(F^2) = 0.255$
$S = 1.13$
3710 reflections
279 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1461P)^2 + 0.054P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.026 (6)
Absolute structure: Flack (1983), 1570 Friedel pairs
Flack parameter: 0.0 (2)

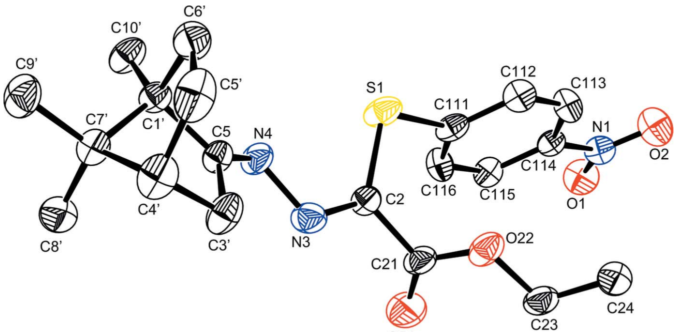


Figure 1
View of (4), showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

The methyl groups were allowed to rotate freely about their C—C bonds, with C—H distances constrained to 0.96 Å and $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(C). All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances equal to 0.93–0.98 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C). Although the standard uncertainty of the Flack (1983) parameter is rather high (Bernardinelli & Flack, 1985), the absolute configuration indicated does agree with the synthetic pathway. The ethyl group is disordered over two positions and the site-occupancy factors were fixed at 0.7:0.3, determined from the refinement. The rather high R values are ascribed to the poor nature of the available crystals.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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