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A chiral 3,4-dihydro-2*H*-thiopyran compound

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.088
Data-to-parameter ratio = 16.4

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

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The title compound, dimethyl (3*R*,4*S*)-3-{[(4*S*)-4-benzyl-2-oxo-1,3-oxazolidin-3-yl]carbonyl}-4-dimethylamino-3,4-dihydro-2*H*-thiopyran-5,6-dicarboxylate, $C_{22}H_{26}N_2O_7S$, is the result of a diastereoselective Diels–Alder reaction between dimethyl (2*E*)-[(dimethylamino)methylene]-3-thiosuccinate and (4*S*)-3-acryloyl-4-benzyl-1,3-oxazolidin-2-one used as chiral auxiliary. Following an X-ray structure determination, the absolute configurations of both stereogenic centres formed during the cycloaddition were determined.

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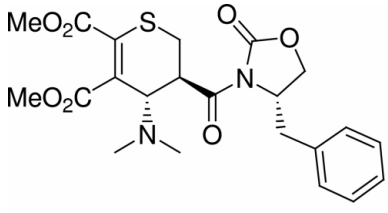
Comment

Asymmetric hetero Diels–Alder reaction appears to be the method of choice for the highly efficient regio- and stereoselective synthesis of various heterocycles in enantiomerically pure form (Waldmann, 1994). In the course of an ongoing project (Trippé *et al.*, 2002) and in view of previous results obtained in our laboratory (Marchand *et al.*, 1995), we isolated the substituted dihydro-2*H*-thiopyran resulting from the [4+2] cycloaddition reaction of dimethyl (2*E*)-[(dimethylamino)methylene]-3-thiosuccinate (Tea Gokou *et al.*, 1985) and (4*S*)-3-acryloyl-4-benzyl-1,3-oxazolidin-2-one (Evans *et al.*, 1984) in the presence of $MgBr_2$ as catalyst. Only two diastereoisomers, in a 7/3 ratio, were obtained at the end of the reaction and these were separated by chromatography on SiO_2. The major component is the title compound, (I), and is the result of an *exo* transition-state topography in the cycloaddition, whereas the minor component is presumed to come from an *endo* approach. A full report on the synthesis, as well as structural and mechanistic studies, will be published separately. Atoms O5, C12, N2, C13 and O6 are coplanar within less than 0.09 Å.



(I)

Experimental

To a suspension of activated magnesium turnings (3.25 mmol) in dry Et_2O was added 1,2-dibromoethane (3.25 mmol). The resulting mixture was stirred until all magnesium turnings disappeared and the solvent was evaporated under an N_2 stream. After addition of dry CH_2Cl_2 (10 ml), (4*S*)-3-acryloyl-4-benzyl-1,3-oxazolidin-2-one (1.10 mmol) in anhydrous CH_2Cl_2 (3 ml) was added at 263 K. After

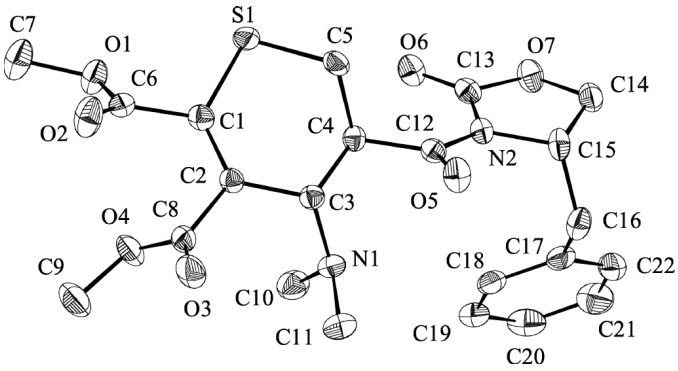


Figure 1
The molecular structure of (I), shown with 50% probability displacement ellipsoids. H atoms are omitted for clarity.

stirring at 263 K for 15 min, dimethyl (2*E*)-[(dimethylamino)-methylene]-3-thiosuccinate (1.10 mmol) was slowly added. The reaction mixture was then stirred at 263 K for 3 h. Saturated $NaHCO_3$ (5 ml) was added and the organic layer was washed with saturated $NaHCO_3$ (2 × 5 ml), water (5 ml) and brine (5 ml). The CH_2Cl_2 extract was then dried over anhydrous $MgSO_4$, filtered and concentrated. The crude mixture was flash-chromatographed on silica (eluent: petroleum ether/AcOEt, 7:3) to afford (I) (285 mg, 57%), along with one other diastereoisomer (142 mg, 28%). Single crystals of (I) suitable for X-ray analysis were obtained by crystallization from AcOEt/petroleum ether.

Crystal data

$C_{22}H_{26}N_2O_7S$
M_r = 462.5
Orthorhombic, $P2_12_12_1$
a = 6.1205 (1) Å
b = 16.1195 (4) Å
c = 22.9272 (6) Å
V = 2261.98 (9) Å^3
Z = 4
D_x = 1.358 Mg m^{-3}
Mo Kα radiation
Cell parameters from 14696 reflections
θ = 2.9–26.7°
μ = 0.19 mm^{-1}
T = 150 K
Needle, colourless
0.40 × 0.03 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: none
22365 measured reflections
4753 independent reflections
3833 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 26.7°
$h = -7 \rightarrow 6$
$k = -20 \rightarrow 20$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$= 0.043
$wR(F^2)$ = 0.088
S = 1.23
4753 reflections
290 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(I) + 0.001296I^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.76 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}
Extinction correction: B–C type 1 Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 1.5 (2)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (8)

All non-H atoms were refined with anisotropic atomic displacement parameters. The orientation of the CH_3 groups was determined from difference Fourier syntheses and they were initially refined as rigid bodies. All H atoms were then fixed at calculated and/or refined positions. A riding isotropic displacement parameter was used for all H atoms. The absolute configuration was unambiguously determined by refining the Flack enantiopole parameter using 1994 Friedel pairs.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995); program(s) used to refine structure: *JANA*2000 (Petricek & Dusek, 2000); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *JANA*2000.

References

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* A**30**, 129–153.
Brandenburg, K & Berndt, M. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Evans, D. A., Chapman, K. T., Bisaha, J. (1984). *J. Am. Chem. Soc.* 106, 4261–4263.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Marchand, A., Mauger, D., Guingant, A. & Pradère, J.-P. (1995). *Tetrahedron Asymmetry*, **6**, 4, 853–856.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
Petricek, V. & Dusek, M. (2000). *JANA*2000. Institute of Physics, Praha, Czech Republic.
Sheldrick, G. M. (1995). *SHELXTL*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Tea Gokou, C., Pradère, J.-P. & Quiniou, H. (1985). *J. Org. Chem.* 50, 1545–1547.
Trippé, G., Perron, J., Harrison-Marchand, A., Dupont, V., Guingant, A., Pradère, J.-P. & Toupet, L. (2002). *Tetrahedron Lett.* **43**, 6067–6069.
Waldmann, H (1994). *Synthesis*, 535–551.