Acta Crystallographica Section E
Structure Reports Online

ISSN 1600-5368

Ethyl 3-(1-benzoyl-3-phenylaziridin-2-yl)-propenoate

Andrei S. Batsanov,[a]* William M. Dutton,[a] Patrick G. Steel[a] and David J. Aldous[b]

[a]Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England, and [b]Aventis Pharma Inc., Route 202-206, Bridgewater, PO Box 6800, New Jersey 08807, USA

Correspondence e-mail:
a.s.batsanov@durham.ac.uk

Received 7 March 2003
Accepted 14 March 2003
Online 21 March 2003

Key indicators

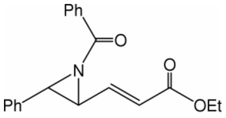
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.097
Data-to-parameter ratio = 13.2

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

The title compound, $C_{20}H_{19}NO_3$, has a strongly pyramidal aziridine N atom, not conjugated with the adjacent C=O bond.

Comment

The title compound, (I), was prepared in the course of our studies of thermal rearrangements of vinyl epoxides and vinyl aziridines (Aldous *et al.*, 1999), by a one-pot modification of literature methods for the aziridine formation and subsequent protection, *e.g.* described for the parent NH aziridine by Wipf & Fritch (1994) and Coldham *et al.* (1995).



(I)

The ethylpropenoate chain, C2′/C3/C2/C1/O1/O2/C4/C5, is planar with a mean atomic deviation of 0.04 Å. It forms a dihedral angle of 74.4 (1)° with the aziridine ring plane. With respect to the latter, the phenyl substituent at C3′ is *trans* and the benzoyl substituent at N1′ is *cis* to the ethylpropenoate group.

The N1′ atom is strongly pyramidal, with the sum of valence angles 308.2 (3)° (*cf* 360° for the ideally planar and 328.5° for tetrahedral geometry). The out-of-(aziridine)plane tilt of the N1′—C6 bond (Ohwada *et al.*, 1998) is 50.3 (1)°. In this respect, (I) is similar to other acylaziridine derivatives (Zacharis & Trefonas, 1968; Gopalakrishna, 1972; Brzozowski *et al.*, 1988; Ferraris *et al.*, 1998), but different from acyclic tertiary amides, where the N atom is always planar-trigonal and its lone electron pair is conjugated with the carbonyl group. In (I), the 'torsion angle' (around the N1′—C6 bond) between the directions of the N1′ lone pair and the C6 $p\pi$ orbital does not exceed 16°, *i.e.* is compatible with conjugation. Nevertheless, the N1′—C6 bond distance of 1.395 (2) Å in (I), while comparable with the range of 1.383–1.388 Å in previously reported acylaziridines (see above), is considerably longer than in acyclic amides with two sp^3 C atoms bonded to the N atom [average 1.346 (10) Å (Chakrabarti & Dunitz, 1982) or 1.352 (10) Å (Allen *et al.*, 1987)]. The amides, in which the N atom is incorporated into a larger ring, *e.g.* a proline ring, show even shorter C(O)—N bonds, averaging 1.335 (9) Å (Chakrabarti & Dunitz, 1982).

The geometry of the aziridine ring is similar to that previously observed (*e.g.* Ohwada *et al.*, 1998). It agrees also with the results of a microwave study of free aziridine, C_2H_5N, in the gas phase by Turner *et al.* (1955).

DOI: 10.1107/S1600536803005981

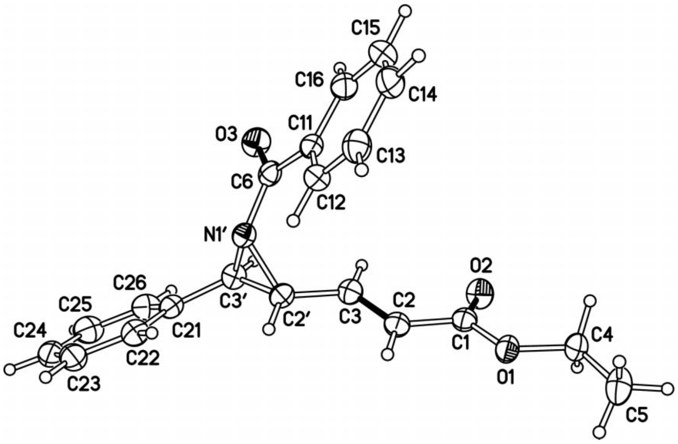


Figure 1
The molecular structure of (I). Atomic displacement ellipsoids are drawn at the 50% probability level and double bonds are shown in black.

Experimental

The azide alcohol $PhCH(OH)CH(N_3)C{=}CCO_2Et$ (2.48 g, 9.51 mmol) in dichloromethane, DCM (10 ml) was added dropwise to a stirred solution of PPh_3 (3.41 mg, 13.1 mmol) at 273 K. Acetic acid (100 µl) in DCM (5 ml) was added under argon. The reaction mixture was warmed to room temperature over 3 h; after 1 h it was cooled to 273 K and triethylamine (4 g, 40 mmol) was added until the pH increased to 8 (measured using universal testing paper). Benzoyl chloride was added (1.4 g, 10 mmol) and the reaction mixture was stirred for 18 h while warming to room temperature. The mixture was washed with water (2 × 30 ml) and the aqueous washings back-extracted with DCM (30 ml). The combined organic layers were dried ($MgSO_4$), the solvent removed and product purified by flash chromatography (eluting with 10% ethyl acetate in petrol) to yield the title amide, (I), as a colourless crystalline solid (1.32 g, 44%). M.p. 390.7–391.1 K. Analysis calculated for $C_{20}H_{19}NO_3$: C 74.7, H 5.92, N 4.36%; found: C 74.71, H 5.96, N 4.51. IR, ν (cm^{-1}): 1710 and 1654 (C═O), 1623 (C═C), 1447, 1297, 1257. ^1H NMR (δ, p.p.m., 400 MHz): 7.96 (2H, *d*, J = 6.8 Hz, *o*-Ph), 7.3–7.6 (8H, *m*, Ph), 6.44 (1H, *dd*, J = 10 Hz, 16 Hz, H3), 6.14 (1H, *d*, J = 16 Hz, H2), 4.13 (2H, *q*, J = 7 Hz, CH_2), 3.83 (1H, *d*, J = 2.4 Hz, H3′), 3.43 (1H, *dd*, J = 10 Hz, 2.4 Hz, H2′), 1.23 (3H, *t*, J = 7 Hz, Me). ^{13}C NMR (δ, p.p.m., 100 MHz): 176 (C6), 165 (C1), 143 (C2), 135, 133, 132, 130, 129, 128, 128, 126 (Ph), 125 (C3), 60 (C3′), 49 (C2′), 47 (C4), 14 (C5). m/z (CI/NH_3): 322 (M^+ + H, 33%), 276, 248, 216, 105 (100%).

Crystal data

$C_{20}H_{19}NO_3$
$M_r = 321.36$
Monoclinic, $P2_1/c$
$a = 10.746\ (1)$ Å
$b = 14.319\ (1)$ Å
$c = 10.998\ (1)$ Å
$\beta = 93.52\ (1)^\circ$
$V = 1689.1\ (2)$ Å^3
$Z = 4$
$D_x = 1.264$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 499 reflections
$\theta = 10.2–20.9^\circ$
$\mu = 0.09$ mm^{-1}
$T = 150\ (2)$ K
Block, colourless
0.4 × 0.3 × 0.2 mm

Data collection

SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan *SADABS*; Sheldrick, 1998)
$T_{min} = 0.757$, $T_{max} = 1.000$
17984 measured reflections
3880 independent reflections
2850 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 27.5^\circ$
$h = -13 \rightarrow 13$
$k = -18 \rightarrow 16$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.097$
$S = 1.09$
3880 reflections
294 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2 + 0.6441P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0099 (9)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3432 (18)	C1—C2	1.476 (2)
O1—C4	1.4577 (18)	C2—C3	1.323 (2)
O2—C1	1.2087 (18)	C2′—C3	1.468 (2)
O3—C6	1.2246 (17)	C2′—C3′	1.514 (2)
N1′—C6	1.3953 (19)	C3′—C21	1.490 (2)
N1′—C3′	1.4620 (19)	C4—C5	1.501 (2)
N1′—C2′	1.4745 (19)	C6—C11	1.493 (2)
C1—O1—C4	115.89 (12)	N1′—C2′—C3′	58.56 (9)
C6—N1′—C3′	121.45 (12)	C2—C3—C2′	122.97 (14)
C6—N1′—C2′	124.68 (12)	N1′—C3′—C21	117.27 (13)
C3′—N1′—C2′	62.08 (9)	N1′—C3′—C2′	59.36 (9)
O2—C1—O1	124.01 (14)	C21—C3′—C2′	122.77 (13)
O2—C1—C2	125.83 (14)	O1—C4—C5	106.65 (14)
O1—C1—C2	110.16 (12)	O3—C6—N1′	121.39 (14)
C3—C2—C1	121.56 (14)	O3—C6—C11	122.10 (14)
C3—C2′—N1′	119.17 (13)	N1′—C6—C11	116.25 (12)
C3—C2′—C3′	118.76 (13)		

All H atoms were located in a difference Fourier synthesis and were refined in isotropic approximation. Bond lengths: Csp^2—H = 0.97 (1) and 0.98 (1) Å, Csp^3—H = 0.96 (2)–1.03 (2) Å, O—H = 0.82 (4) and 0.84 (4) Å.

Data collection: *SMAR*T (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

References

Aldous, D. J., Dutton, W. M. & Steel, P. G. (1999). *Synlett*, pp. 474–476.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Bruker (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Brzozowski, A. M., Grabowski, M. J., Stepien, A. & Dauter, Z. (1988). *Acta Cryst.* C**44**, 332–334.
Chakrabarti, P. & Dunitz, J. D. (1982). *Helv. Chim. Acta*, **65**, 1555–1562.
Coldham, I., Collis, A. J., Mould, R. J. & Robinson, D. E. (1995). *Synthesis*, pp. 1147–1150.
Ferraris, D., Drury, W. J. III, Cox, C. & Lectka, T. (1998). *J. Org. Chem.* **63**, 4568–4569.
Gopalakrishna, E. M. (1972). *Acta Cryst.* B**28**, 2754–2759.
Ohwada, T., Achiva, T., Okamoto, I., Shudo, K. & Yamaguchi, K. (1998). *Tetrahedron Lett.* pp. 865–868.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Sheldrick, G. M. (1998). *SADABS*. University of Göttingen, Germany.
Siemens (1995). *SMART* and *SAINT*. Versions 6.01. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Turner, T. E., Fiora, V. C. & Kendrick, W. M. (1955). *J. Chem. Phys.* **23**, 1966.
Wipf, P. & Fritch, P. C. (1994). *J. Org Chem.* **59**, 4875–4886.
Zacharis, H. M. & Trefonas, L. M. (1968). *J. Heterocycl. Chem.* **5**, 343–349.