References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Rae, A. D., Craig, D. C., Dance, I. G., Scudder, M. L., Dean, P. A. W., Kmetic, M. A., Payne, N. C. & Vittal, J. J. (1997). *Acta Cryst.* B**53**, 457–465.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1983). *R3M Software*. Version 4.11. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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3-Diazo-1-benzyloxycarbonylpyrrolidin-2-one[†]

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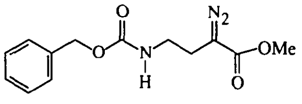
Abstract

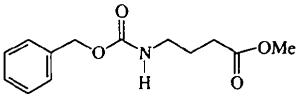
The title compound, $C_{12}H_{11}N_3O_3$, was an unexpected reaction product. It is a rare example of a cyclic diazo amide and is a potential precursor for important azetidine derivatives *via* Wolff rearrangement.

Comment

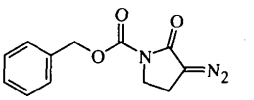
In an attempt to prepare 2-diazo-4-benzyloxycarbonylaminobutyric acid methyl ester, (1), from 4-benzyloxycarbonylaminobutyric acid methyl ester, (2), according to a modified Danheiser diazo-transfer procedure (Danheiser, Miller, Brisbois & Park, 1990) described below, we isolated as a by-product 3-diazo-1-benzyloxycarbonylpyrrolidin-2-one, (3), presumed to be the *in situ* product of cyclization of (1). A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed that, of the 22 recorded crystal and molecular structures of diazocarbonyl compounds, five are cyclic molecules but none is a diazopyrrolidinone. As cyclic diazocarbonyl compounds are of considerable use as intermediates in modern organic synthesis (Ye & McKervey, 1994; Doyle, Ye & McKervey, 1997), especially in Wolff rearrangement, we have determined the crystal and molecular structure of (3) by X-ray diffraction.



(1)



(2)



(3)

The molecule (Fig. 1) consists of two broadly planar sections (saturated C atoms notwithstanding), with the phenyl ring inclined to the mean plane of the rest of the molecule at 44.69 (3)°. There is evidence of π–π interactions between the phenyl ring and the diazocarbonyl group of an adjacent molecule at ($\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$). The vertical distance between the phenyl plane and that of the diazo group is *ca* 3.2 Å and the two π systems show the expected offset arrangement.

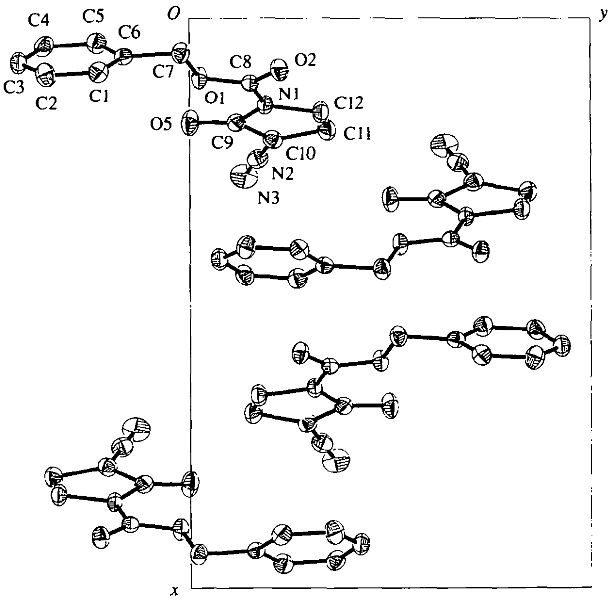


Fig. 1. A view of the unit cell projected along **z**, showing the disposition of the π systems of the phenyl and diazo groups in adjacent molecules. Atoms are represented by 50% probability displacement ellipsoids and H atoms have been omitted for clarity.

Experimental

A 100 ml two-necked round-bottomed flask equipped with a rubber septum and a 25 ml pressure-equalizing addition funnel containing an Ar atmosphere was charged with a solution of 1,1,1,3,3,3-hexamethyldisilazane (6.69 mmol, 1.079 g, 1.41 ml)

[†] IUPAC name: benzyl 3-diazo-2-oxopyrrolidine-1-carboxylate.

in THF (20 ml) and then cooled at 273 K while *n*-butyllithium solution (1.6 *M* in hexane, 6.85 mmol, 4.3 ml) was added dropwise. After 1 h, the resulting solution was cooled at 195 K while a solution of 4-benzyloxycarbonylaminobutyric acid methyl ester (1.67 mmol, 0.42 g) in THF (10 ml) was added dropwise over 20 min. The reaction mixture was stirred at 195 K for 1 h, warmed slowly to 243 K over a period of 2 h before being cooled again to 195 K. Then 2,2,2-trifluoroethyl trifluoroacetate (3.34 mmol, 0.655 g, 0.45 ml) was added in one portion. The reaction mixture was allowed to warm to 223 K over 1 h and the solvent was then removed. The resulting mixture was poured into a separatory funnel containing 1 *M* HCl (30 ml) and Et_2O (30 ml). The aqueous phase was extracted with two 20 ml portions of Et_2O and the combined organic phases were then washed with saturated NaCl solution (30 ml) and concentrated at reduced pressure to give a straw-coloured oil which was immediately dissolved in CH_3CN (30 ml) and transferred to a 100 ml two-necked round-bottomed flask equipped with a rubber septum and a 25 ml pressure-equalized addition funnel containing an Ar atmosphere. Et_3N (8.36 mmol, 0.85 g, 1.2 ml) was added and a solution of tosyl azide (8.36 mmol, 1.65 g) in CH_3CN (10 ml) added dropwise over 20 min. The resulting solution was stirred at room temperature for 16 h and then concentrated to a volume of *ca* 5 ml. The residue was dissolved in Et_2O (30 ml) and washed with H_2O (3×25 ml) and saturated NaCl solution (25 ml). The organic phase was then dried over Na_2SO_4, filtered and concentrated to afford 1.463 g of a yellow oil. Column chromatography on silica gel (elution with 20% ethyl acetate/hexane) afforded the desired compound (1) followed by 70 mg (20%) of diazocarbonyl compound (3) as a yellow crystalline solid. Preliminary purification of (3) was by flash chromatography, following which suitable crystals were grown from methanol (m.p. 331–333 K). ^1H NMR ($CDCl_3$, 300 MHz): 7.45–7.32 (*m*, 5H, ArH), 5.29 (*s*, 2H, OCH_2), 3.87–3.82 (*m*, 2H, NCH_2), 3.13–3.08 p.p.m. (*m*, 2H, CH_2). IR ν_{max} (KBr disc): 2346 cm^{-1} (diazo). High resolution MS calculated for $C_{12}H_{11}N_3O_3$ (M^+) 245.0814; found 245.0810.

Crystal data

$C_{12}H_{11}N_3O_3$
$M_r = 245.24$
Orthorhombic
$Pna2_1$
$a = 15.3090\,(7)$ Å
$b = 10.5530\,(11)$ Å
$c = 6.9730\,(14)$ Å
$V = 1126.5\,(2)$ Å^3
$Z = 4$
$D_x = 1.446$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 34 reflections
$\theta = 5.0$–$12.5°$
$\mu = 0.107$ mm^{-1}
$T = 153\,(2)$ K
Wedge
$0.95 \times 0.45 \times 0.15$ mm
Yellow

Data collection

Siemens *P*4 four-circle diffractometer
ω scans from $(K_{\alpha 1} - 0.6)$ to $(K_{\alpha 2} + 0.6)$
Absorption correction: none
1506 measured reflections
1260 independent reflections
1170 reflections with $I > 2\sigma(I)$

$R_{int} = 0.010$
$\theta_{max} = 25°$
$h = -8 \rightarrow 18$
$k = -12 \rightarrow 1$
$l = -8 \rightarrow 8$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.069$
$S = 1.123$
1260 reflections
164 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.0716P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.13$ e Å^{-3}

Extinction correction: *SHELXL*93
Extinction coefficient: 0.0174 (19)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.7 (13) (polarity not determined)

Table 1. *Selected geometric parameters (Å, °)*

N1—C9	1.411 (3)	C10—N2	1.301 (3)
N1—C12	1.486 (2)	C10—C11	1.494 (3)
C9—O5	1.222 (2)	N2—N3	1.130 (3)
C9—C10	1.437 (3)	C11—C12	1.537 (3)
C8—N1—C9	129.7 (2)	N2—C10—C9	120.1 (2)
C8—N1—C12	117.6 (2)	N2—C10—C11	125.7 (2)
C9—N1—C12	112.6 (2)	C9—C10—C11	114.2 (2)
O5—C9—N1	126.9 (2)	N3—N2—C10	178.9 (2)
O5—C9—C10	128.4 (2)	C10—C11—C12	101.6 (2)
N1—C9—C10	104.7 (2)	N1—C12—C11	105.7 (2)

The structure was solved by direct methods (Sheldrick, 1990*a*). All the non-H atoms were refined with anisotropic atomic displacement parameters. H atoms were inserted at calculated positions with isotropic displacement parameters riding on U^{ij} of the carrier atoms. The absolute structure was not determined.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1160). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

Danheiser, R. L., Miller, R. F., Brisbois, R. G. & Park, S. Z. (1990). *J. Org. Chem.* **55**, 1959–1964.

Doyle, M. P., Ye, T. & McKervey, M. A. (1997). In *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*. New York: John Wiley. In the press.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1990*b*). *SHELXTL/PC Users Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Ye, T. & McKervey, M. A. (1994). *Chem. Rev.* **94**, 1091–1160.