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# Ethyl 2-benzyl-2-nitro-3-phenylpropanoate

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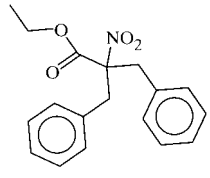
The title compound, $C_{18}H_{19}NO_4$, is the key synthetic intermediate in the preparation of $\alpha,\alpha$-dibenzyl-$\alpha$-amino acid (dibenzylglycine, Dbg), the disubstituted homologue of phenylalanine, following the dialkylation of ethyl nitroacetate. The molecule does not have its potential mirror symmetry in the crystal, with the two benzyl groups forming N—C—C—C torsion angles of 60.31 (13) and 79.89 (13)°.

## Comment

The ability of $\alpha,\alpha$-disubstituted-$\alpha$-amino acids to modulate the chemical and physical properties of peptides (Olson *et al.*, 1990) has given rise to an increased interest in their synthesis and subsequent incorporation into peptides (Trost & Arisa, 1997; Dyker, 1997). One synthon of particular interest to the preparation of amino acids, as well as to other compounds of biological relevance, is the alkyl nitroacetates (Shipchandler, 1979). For the synthesis of mono- and disubstituted $\alpha$-amino acids from these precursors, the ability to undergo electrophilic substitution reactions at the $\alpha$-methylene of nitroacetate is of primary importance. However, the synthesis of the title compound, (I), representing dialkylation at this position, as




(I)

opposed to competing *O*-alkylation, has previously required two separate synthetic steps to accomplish in moderate yield (Gogte *et al.*, 1987). We have conducted the synthesis in one synthetic step, and herein the structure of the title compound is reported. Further structural comparisons with other $\alpha,\alpha$-disubstituted alkyl nitroacetates, as well as their conversion to novel prochiral $\alpha,\alpha$-disubstituted glycines, will be reported elsewhere (Fu *et al.*, 2000).

The molecule potentially has mirror symmetry; however, it is crystallographically asymmetric, with benzyl groups forming torsion angles of the same sign with the nitro N atom, N1—C1—C5—C6 60.31 (13)° and N1—C1—C12—C13 79.89 (13)°. One is *anti* to the ester substituent [C2—C1—C5—C6 177.05 (10)°] while the other is more nearly *syn* [C2—C1—C12—C13 −38.54 (14)°]. The phenyl rings thus form a dihedral angle of 74.04 (7)°.

## Experimental

Benzyl bromide (2.7 g, 15.8 mmol) was added to a mixture of ethyl nitroacetate (1.0 g. 7.5 mmol), tetrabutylammonium bromide (0.24 g, 0.75 mmol) and diisopropylethylamine (2.0 g, 15.8 mmol) dissolved in 5 ml of dry dimethylformamide. The reaction was stirred for 2 h, and the precipitated diisopropylethylammonium bromide salt was removed by filtration and washed with diethyl ether (100 ml). The resulting filtrate was washed with water (5 × 50 ml). The organic layer was dried over sodium sulfate, filtered, and the ether removed by evaporation at 273 K to provide a yellow oil (2.0 g, 88% crude yield). Silica-gel column chromatography with pentane/diethyl ether provided a white crystalline solid following removal of solvents (1.48 g, 63% yield). The compound was crystallized (in the dark under argon) from hot pentane by slow cooling.

*Crystal data*

| | |
|---|---|
| $C_{18}H_{19}NO_4$ | $D_x$ = 1.292 Mg m$^{-3}$ |
| $M_r$ = 313.34 | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 7336 reflections |
| $a$ = 18.0850 (6) Å | $\theta$ = 2.5–27.5° |
| $b$ = 6.0670 (2) Å | $\mu$ = 0.091 mm$^{-1}$ |
| $c$ = 15.9830 (6) Å | $T$ = 120 K |
| $\beta$ = 113.280 (2)° | Lath, colourless |
| $V$ = 1610.90 (10) Å$^3$ | 0.50 × 0.10 × 0.05 mm |
| $Z$ = 4 | |

*Data collection*

| | |
|---|---|
| KappaCCD diffractometer (with Oxford Cryosystems Cryostream cooler) | 2576 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.038 |
| | $\theta_{max}$ = 27.5° |
| $\omega$ scans with $\kappa$ offsets | $h = -23 \rightarrow 23$ |
| 7336 measured reflections | $k = -7 \rightarrow 7$ |
| 3662 independent reflections | $l = -20 \rightarrow 20$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 0.1307P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)]$ = 0.039 | |
| $wR(F^2)$ = 0.094 | |
| $S$ = 1.037 | $(\Delta/\sigma)_{max}$ = 0.001 |
| 3662 reflections | $\Delta\rho_{max}$ = 0.27 e Å$^{-3}$ |
| 210 parameters | $\Delta\rho_{min}$ = −0.22 e Å$^{-3}$ |
| H-atom parameters constrained | Extinction correction: *SHELXL*97 |
| | Extinction coefficient: 0.0152 (17) |

H atoms were placed in calculated positions with C—H bond distances of 0.95 Å for phenyl, 0.99 Å for methylene and 0.98 Å for methyl, and thereafter treated as riding. A torsional parameter was refined for the methyl group. $U_{iso} = 1.2U_{eq}$ of the attached C atom (1.5 for methyl groups).

Data collection: *KappaCCD Software* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPAK*; data reduction: *DENZO* and *SCALEPAK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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## References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Dyker, G. (1997). *Angew. Chem. Int. Ed. Engl.* **36**, 1700–1702, and references therein.

Fu, Y., Miller, T. J., Hammarström, L. G. J., McLaughlin, M. L. & Hammer, R. P. (2000), *Tetrahedron Lett.* Submitted.

Gogte, V. N., Natu, A. A. & Pore, V. S. (1987). *Synth. Commun.* **17**, 1421–1429.

Nonius (1998). *KappaCCD Software*. Nonius BV, Delft, The Netherlands.

Olson, G. L., Voss, M. E., Hill, D. E., Kahn, M., Madison, V. S. & Cook, C. M. (1990). *J. Am. Chem. Soc.* **112**, 323–333.

Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Shipchandler, M. T. (1979). *Synthesis*, pp. 666–686.

Trost, B. M. & Arisa, X. (1997). *Angew. Chem. Int. Ed. Engl.* **36**, 2635–2637, and references therein.