

*Crystal data*C₁₅H₂₁N₃O₃S $M_r = 323.41$

Monoclinic

 $P2_1/n$ $a = 10.8326 (7) \text{ \AA}$ $b = 14.3281 (15) \text{ \AA}$ $c = 10.976 (3) \text{ \AA}$ $\beta = 107.026 (11)^\circ$ $V = 1628.9 (4) \text{ \AA}^3$ $Z = 4$ $D_x = 1.319 \text{ Mg m}^{-3}$ D_m not measuredCu $K\alpha$ radiation $\lambda = 1.54178 \text{ \AA}$

Cell parameters from 25 reflections

 $\theta = 20\text{--}30^\circ$ $\mu = 1.906 \text{ mm}^{-1}$ $T = 293 (1) \text{ K}$

Block

 $0.30 \times 0.26 \times 0.18 \text{ mm}$

Colorless

Data collection

Enraf–Nonius CAD-4

diffractometer

 $\omega/2\theta$ scans

Absorption correction:

 ψ scans (North *et al.*, 1968) $T_{\min} = 0.654$, $T_{\max} = 0.710$

3018 measured reflections

2871 independent reflections

2345 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.026$ $\theta_{\max} = 68.0^\circ$ $h = 0 \rightarrow 13$ $k = 0 \rightarrow 17$ $l = -12 \rightarrow 12$

3 standard reflections

every 200 reflections

intensity decay: 1.48%

*Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.053$ $wR(F^2) = 0.149$ $S = 1.019$

2871 reflections

201 parameters

H atoms constrained

 $w = 1/[\sigma^2(F_o^2) + (0.09P)^2]$ $+ 0.65P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.605 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.210 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)Table 1. Selected geometric parameters ($\text{\AA}$, $^\circ$)

S1—O1	1.419 (2)	N1—C1	1.394 (3)
S1—O2	1.427 (2)	N2—C1	1.333 (3)
S1—N1	1.634 (2)	N2—N3	1.414 (3)
S1—C2	1.758 (3)	N3—C9	1.465 (3)
O3—C1	1.218 (3)	N3—C15	1.473 (4)
O1—S1—O2	119.46 (12)	C1—N1—S1	124.6 (2)
O1—S1—N1	108.59 (12)	C1—N2—N3	121.6 (2)
O2—S1—N1	103.22 (11)	N2—N3—C9	111.3 (2)
O1—S1—C2	108.88 (12)	N2—N3—C15	109.8 (2)
O2—S1—C2	108.56 (12)	C9—N3—C15	104.1 (2)
N1—S1—C2	107.48 (11)		

Table 2. Hydrogen-bonding geometry ($^\circ$, $\text{\AA}$)

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N1—H1 $\cdots$ O2 ⁱ	0.86	2.23	2.967 (3)	143
N2—H2 $\cdots$ O3 ⁱⁱ	0.86	2.15	2.949 (3)	153

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 - x, 1 - y, 1 - z$.

The space group was uniquely determined from the systematic absences.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics:

ORTEP in *TEXSAN*. Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1499). Services for accessing these data are described at the back of the journal.

References

- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Fan, H.-F. (1991). *SAPI91. Structure Analysis Program with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kamenar, B., Matkovic, D. & Nagl, A. (1983). *Croat. Chem. Acta*, **56**, 87–95.
- Koo, C. H., Suh, J. S., Yeon, Y. H. & Watanabe, T. (1988). *Arch. Pharm. Res.* **11**, 74–79.
- Lebovitz, H. E. & Feinglos, M. N. (1983). *Diabetes Mellitus: Theory and Practices*, 3rd ed., edited by M. Ellenberg & H. Rifkin, pp. 591–610. New York: Medical Examination Publishing.
- Long, J. W. (1990). *The Essential Guide to Prescription Drugs*, pp. 505–509. New York: Harper & Row.
- Molecular Structure Corporation (1994). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Reynolds, J. E. F. (1994). *Martindale: The Extra Pharmacopoeia*, 13th ed., p. 279. London: Info Access & Distribution Pte Ltd.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Stockley, I. H. (1991). *Drug Interactions*, 2nd ed., pp. 417–426. London: Blackwell Scientific Publication.
- Webster, J. M. & Taylor, R. (1996). *Diab. Nutr. Metab.* **9**, 115–121.

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N—H $\cdots\pi$ (indole) intermolecular interactions in 3,3'-benzylidenediindole

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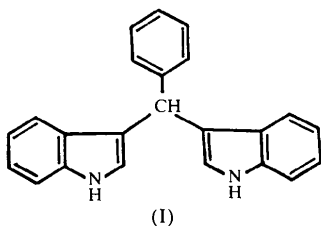
Abstract

In molecules of the title compound, C₂₃H₁₈N₂, two indole systems and one phenyl ring are connected through a common C atom. The two indole substituents are mutually orthogonal. We have identified two N—

H $\cdots\pi$ (indole) intermolecular interactions involving different indoles: the H $\cdots$ Cg distances are 2.35 and 2.60 Å (Cg = centroid of six-membered ring of the relevant indole).

Comment

Many indoles show interesting chemical and biological activities. Pharmacological studies of numerous indole derivatives have shown that most of them display anti-inflammatory (Rodriguez *et al.*, 1985) and antimicrobial properties (El-Sayed *et al.*, 1986). The interaction of indole with DNA molecules has been reported (Sivaraman *et al.*, 1996). Here we report the structure of 3,3'-benzylidenediindole, (I).



Both indole moieties are quite planar and are at right angles to each other (Fig. 1). The phenyl ring is perpendicular to indole A [dihedral angle 85.9 (1)°] and makes an angle of 65.5 (1)° with indole B. The twisting of the indole moieties with respect to the phenyl ring can be seen from the torsion angles C9'—C3'—C10—C11—101.0 (2)° and C9—C3—C10—C11 166.4 (2)°. The small tilts between the planes of the five-membered and six-membered rings in indoles A and B are 1.3 (1) and 2.6 (1)°, respectively.

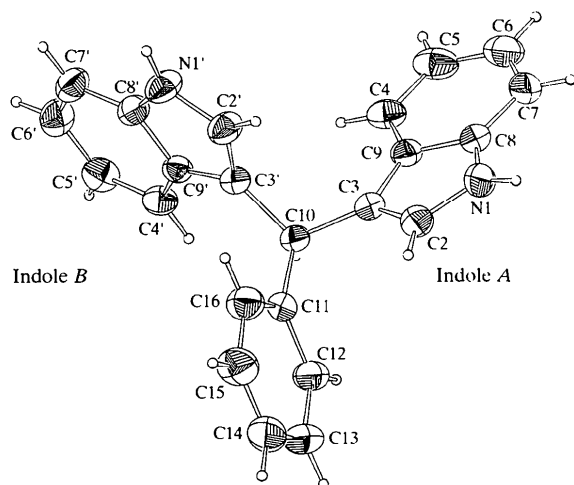


Fig. 1. The molecular structure of the title compound with 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as circles of an arbitrary radius.

Fig. 2 shows the packing of the molecules down the *a* axis and also the presence of two distinct N—H $\cdots\pi$ hydrogen bonds, one of 2.35 Å (H1' $\cdots$ Cg1) with an N1'—H1' $\cdots$ Cg1 angle of 172° and one of 2.60 Å (H1 $\cdots$ Cg2) with an N1—H1 $\cdots$ Cg2 angle of 158° (Table 2). These values agree well with values from the Cambridge Structural Database (Allen *et al.*, 1991) which show that N—H $\cdots\pi$ geometries may be structurally significant when the H $\cdots$ Cg distance is less than 2.6 Å and the N—H $\cdots$ Cg angle is between 130 and 180°.

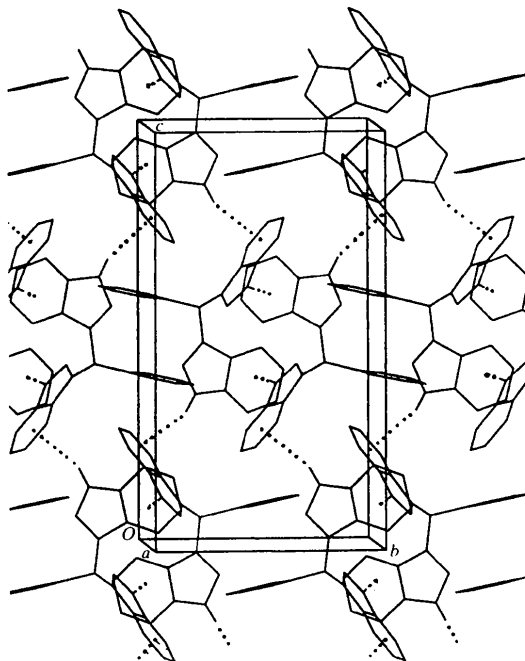


Fig. 2. A view of the molecular packing down the *a* axis.

The H $\cdots$ C range for N1'—H1' $\cdots$ Cg1 is from 2.6 to 2.9 Å and for N1—H1 $\cdots$ Cg2 is from 2.4 to 3.3 Å. Our results may be compared with some H $\cdots$ Cg values for N—H $\cdots\pi$ interactions reported earlier. In a neutron study of vitamin B₁₂ coenzyme there is strong intramolecular hydrogen bonding, with an H $\cdots$ Cg distance of 2.59 Å (Starikov & Steiner, 1998), and for 2- and 3-aminophenols the distance 2.309 Å has been reported (Allen *et al.*, 1997). In an X-ray study of 1,4-bis-(di-2-pyrrolylmethyl)benzene H $\cdots$ Cg distances of 2.42 and 2.52 Å have been reported (Bennis & Gallagher, 1998). This type of amino or amide N—H $\cdots\pi$ aromatic hydrogen-bonding interaction has recently been theoretically postulated in model systems and experimentally described in globular proteins. It has been suggested that such interactions may provide stability, contribute to the folding process or have a functional role in proteins. The molecule is stabilized by the presence of strong N—H $\cdots\pi$ intermolecular interactions (Crisma *et al.*, 1997).

The pattern of N—H...Cg contacts gives rise to infinite double layers of molecules composed of chains running along the *c* direction, each of which is related to two equivalent adjacent chains by inversion.

Experimental

To a solution of methylmagnesium iodide (1.16 g, 7 mmol) in diethyl ether (15 ml) was added indole (0.8 g, 7 mmol) in diethyl ether (12 ml) and stirred at room temperature for 5 min. To the resulting stirred solution of indolylmagnesium iodide were added *N*-benzylideneaniline (0.45 g, 2.5 mmol) and indium trichloride (0.110 g, 0.5 mmol) in MeCN (15 ml). The reaction mixture was stirred for 20 h, then poured into a saturated ammonium chloride solution (20 ml) and extracted with ethyl acetate (3 × 20 ml). The combined extract was dried over sodium sulfate and concentrated under reduced pressure. The residue was chromatographed in a column packed with silica gel and eluted with ethyl acetate/petroleum ether (1:4) to afford 0.6 g (7.5%) of 3,3'-benzylidenediindole. Crystals were grown from the aqueous methanol solution by slow evaporation.

Crystal data

C₂₃H₁₈N₂
 $M_r = 322.39$
 Monoclinic
 $P2_1/c$
 $a = 10.1867(10) \text{ \AA}$
 $b = 9.759(2) \text{ \AA}$
 $c = 17.7778(10) \text{ \AA}$
 $\beta = 94.009(10)^\circ$
 $V = 1763.1(4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.215 \text{ Mg m}^{-3}$
 D_m not measured

Cu K α radiation
 $\lambda = 1.54178 \text{ \AA}$
 Cell parameters from 15 reflections
 $\theta = 2-18^\circ$
 $\mu = 0.550 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Rectangular
 $0.30 \times 0.20 \times 0.15 \text{ mm}$
 Pale brown

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 3331 measured reflections
 3331 independent reflections
 2616 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.044$

Refinement

Refinement on F^2
 $R(F) = 0.053$
 $wR(F^2) = 0.162$
 $S = 1.063$
 3318 reflections
 227 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.137P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.014$

$\theta_{max} = 69.96^\circ$
 $h = 0 \rightarrow 12$
 $k = 0 \rightarrow 11$
 $l = -21 \rightarrow 21$
 3 standard reflections every 200 reflections
 frequency: 60 min
 intensity decay: <1%

$\Delta\rho_{max} = 0.23 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.20 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL93 (Sheldrick, 1993)
 Extinction coefficient: 0.0028(8)
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters ($\text{\AA}$, $^\circ$)

N1—C8	1.360 (3)	N1'—C2'	1.369 (2)
N1—C2	1.369 (3)	N1'—C8'	1.365 (2)
N1—H1	0.86	N1'—H1'	0.86
C8—N1—C2	109.1 (2)	C2'—N1'—C8'	109.06 (14)
C8—N1—H1	125.45 (11)	C2'—N1'—H1'	125.47 (10)
C2—N1—H1	125.45 (11)	C8'—N1'—H1'	125.47 (10)
C3—C2—N1	110.4 (2)	C3'—C2'—N1'	110.4 (2)
N1—C8—C9	107.1 (2)	N1'—C8'—C7'	130.8 (2)
N1—C8—C7	130.8 (2)	N1'—C8'—C9'	107.0 (2)
C9—C3—C10—C11	166.41 (15)	C9'—C3'—C10—C11	-101.0 (2)

Table 2. Hydrogen-bonding geometry ($\text{\AA}$, $^\circ$)

Cg1 is the centroid of the six-membered ring C4—C9 and Cg2 is the centroid of the six-membered ring C4'—C9'.

D—H...A	D—H	H...A	D...A	D—H...A
N1'—H1'...Cg1'	0.86	2.35	3.211 (2)	172
N1—H1...Cg2''	0.86	2.60	3.401 (1)	158

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

H atoms were positioned geometrically and refined using a riding model with N—H 0.86, C—H(aromatic) 0.93 and C—H(aliphatic) 0.98 $\text{\AA}$.

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: SDP (Frenz, 1978). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ZORTEP (Zsolnai, 1997). Software used to prepare material for publication: SHELXL93 and PARST (Nardelli, 1983, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1241). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.
- Allen, F. H., Hoy, V. J., Howard, J. A. K., Thalladi, V. R., Desiraju, G. R., Wilson, C. C. & McIntyre, G. J. (1997). *J. Am. Chem. Soc.* **119**, 3477–3480.
- Bennis, V. & Gallagher, J. F. (1998). *Acta Cryst.* **C54**, 130–132.
- Crisma, M., Formaggio, F., Valle, G., Toniolo, C., Saviano, M., Lacovino, R., Zaccaro, L. & Benedetti, E. (1997). *Biopolymers*, **42**, 1–6.
- El-Sayed, K., Barnhart, D. M., Ammon, H. L. & Wassel, G. M. (1986). *Acta Cryst.* **C42**, 1383–1385.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
- Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft University Press.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Rodríguez, J. G., Temprano, F., Estebancalderon, C., Martinez-Ripoll, M. & Garcíablanco, S. (1985). *Tetrahedron*, **41**, 3813–3815.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
 Sivaraman, J., Subramaniam, K., Velmurugan, D., Subramanian, E. & Seetharaman, J. (1996). *J. Mol. Struct.* **385**, 123–128.
 Starikov, E. B. & Steiner, T. (1998). *Acta Cryst.* **B54**, 94–96.
 Zsolnai, L. (1997). *ZORTEP. An Interactive ORTEP Program for Structure Illustration*. University of Heidelberg, Germany.

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tert-Butoxycarbonyl-L-leucyl-L-threoninamide

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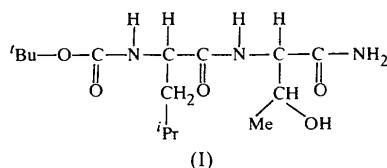
(Received 30 April 1998; accepted 30 July 1998)

Abstract

The peptide chain in C₁₅H₂₉N₃O₅ adopts an extended conformation. The peptide unit is *trans* and shows significant deviations from planarity. The crystal packing enables neighbouring molecules to interact through hydrogen bonding in an anti-parallel fashion.

Comment

The conformation of the *tert*-butoxycarbonyl group in the title peptide, (I), is characterized by the torsion angles $\theta_0 = 175.6(3)^\circ$ (C1—O1—C0'—N1) and $\omega_0 = -173.7(3)^\circ$ (O1—C0'—N1—C1A) as *trans-trans* (Benedetti *et al.*, 1980). The peptide unit is *trans* and shows significant deviation from planarity ($\Delta\omega = 10.7^\circ$). The carboxyl group makes a dihedral angle of 37.5° with the adjacent peptide unit. The peptide chain backbone is folded with the conformation $\varphi_1 = -119.8(3)$, $\psi_1 = 0.9(4)$, $\omega_1 = 169.3(3)$, $\varphi_2 = -139.6(3)$ and $\psi_2 = 161.1(3)^\circ$.



The side chain of the leucyl residue has torsion angles $\chi_1 = -58.9(4)$, $\chi_{21} = 174.4(3)$ and $\chi_{22} = -60.5(5)^\circ$, corresponding to the commonly observed

g[−](*tg*[−]) conformation (Benedetti *et al.*, 1983). The side-chain conformation of the threonyl residue is described by χ_{11} (N2—C2A—C2B—C2G) = $-51.5(3)^\circ$ and χ_{12} (N2—C2A—C2B—O2G) = $73.2(3)^\circ$. For comparison, in Gly—Thr—H₂O, $\chi_{11} = -62$ and $\chi_{12} = 61^\circ$ (Yadava & Padmanabhan, 1973) and in Boc—Phe—D—Leu—Thr—OMe, $\chi_{11} = -69.4(5)$ and $\chi_{12} = 49.9(4)^\circ$ (Doi *et al.*, 1993).

The peptide chain folding introduces an intramolecular interaction [2.629(3) Å] between N2 and O2'. Such an interaction and an accompanying large deviation from planarity of the peptide unit have been observed in other peptides, such as Leu—Leu (Mitra & Subramanian, 1994) and Leu—Ala (Mitra *et al.*, 1996).

The packing gives rise to layers of molecules perpendicular to the *c* axis, with three intermolecular N—H...O hydrogen bonds holding the molecules together in each layer, while the layers are stabilized through hydrophobic and van der Waals interactions.

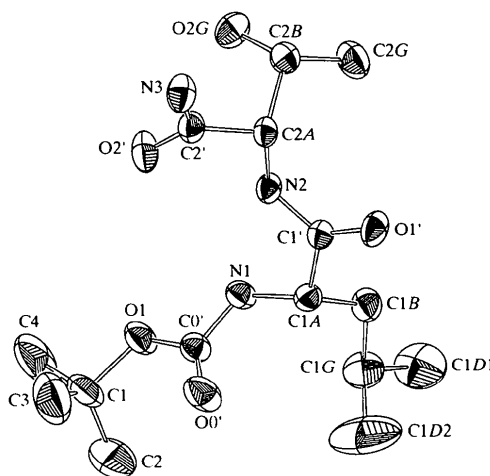


Fig. 1. Perspective view of the molecule, with displacement ellipsoids shown at the 50% probability level. H atoms have been omitted for clarity.

Experimental

The crystals were obtained by slow evaporation of a methanol/water solution at room temperature.

Crystal data

C₁₅H₂₉N₃O₅
 $M_r = 331.41$
 Orthorhombic
 $P2_12_12_1$
 $a = 7.713(2)$ Å
 $b = 8.674(1)$ Å
 $c = 28.325(6)$ Å
 $V = 1895.0(7)$ Å³
 $Z = 4$
 $D_x = 1.162$ Mg m^{−3}
 D_m not measured

Cu $K\alpha$ radiation
 $\lambda = 1.5418$ Å
 Cell parameters from 25 reflections
 $\theta = 15\text{--}22^\circ$
 $\mu = 0.719$ mm^{−1}
 $T = 293(2)$ K
 Parallelepiped
 $0.40 \times 0.28 \times 0.20$ mm
 Colourless