Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

2-(1,2,3,4-Tetrahydrocarbazol-2-yl)butylamine

Tuncer Hökelek,[a]* Süleyman Patır,[b] Yavuz Ergün[c] and Gürol Okay[c]

[a]Department of Physics, Hacettepe University, 06532 Beytepe, Ankara, Turkey, [b]Department of Science, Faculty of Education, Hacettepe University, 06532 Beytepe, Ankara, Turkey, and [c]Department of Chemistry, Hacettepe University, 06532 Beytepe, Ankara, Turkey

Correspondence e-mail:
merzifon@eti.cc.hun.edu.tr

Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
R factor = 0.055
wR factor = 0.157
Data-to-parameter ratio = 14.8

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

Received 11 May 2001
Accepted 31 May 2001
Online 15 June 2001

The title compound, $C_{16}H_{22}N_2$, consists of a carbazole skeleton with a butylamine side chain at position 2. Molecules are linked about inversion centres by N—H···N hydrogen bonds [N···N 2.950 (3) Å] to form centrosymmetric dimers.

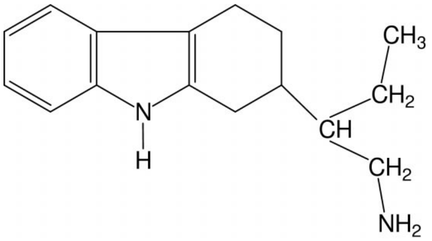
Comment

1,2,3,4-Tetrahydrocarbazole derivatives can be considered to be synthetic precursors of tetracyclic indole alkaloids. They have tricyclic ring systems with the rings named as *A*, *B* and *C* as in the strychnose type of indole alkaloids (Bosch & Bonjoch, 1988). The possibility of synthesizing the indole type of alkaloids by substitution at different positions is currently under investigation (Patır *et al.*, 1997).

Tetrahydrocarbazole systems are present in the framework of a number of indole-type alkaloids of biological interest (Phillipson & Zenk, 1980; Saxton, 1983; Abraham, 1975).

The structures of tetrahydrocarbazole derivatives having different substituents at different positions of the carbazole core, *e.g.* 4-methylcarbazole-3-carboxylic acid, (II) (Hökelek *et al.*, 2001), 1-benzyloxy-1,2,3,4-tetrahydrocarbazole, (III) (Hökelek *et al.*, 2000), *N*-(1,2,3,4-tetrahydrocarbazole-1-yl)-2-methoxyacetamide, (IV) (Hökelek & Patır, 2000*a*), 2,3-dihydro-3-ethyl-9-(phenylsulfonyl)carbazol-4(1*H*)-one, (V) (Hökelek & Patır, 2000*b*), *N*-(2,2-dimethoxyethyl)-*N*-(9-methoxymethyl-1,2,3,4-tetrahydrospiro[carbazole- 1,2′-[1,3]-dithiolan]-4-yl)benzamide, (VI) (Hökelek & Patır, 1999) and 1,2,3,4-tetrahydrocarbazole-1-spiro-2′-[1,3]dithiolane, (VII) (Hökelek *et al.*, 1994) have been the subject of much interest in our laboratory.

The title compound, (I), may be an interesting intermediate in the synthesis of tetracyclic indole alkaloids (Magnus *et al.*, 1992).



(I)

The present structure determination of (I) was undertaken in order to understand the effects of the butylamine side chain at position 2 on the geometry of the carbazole system, and to compare the results with those of previously reported tetrahydrocarbazole derivatives.

DOI: 101107/S1600536801008984

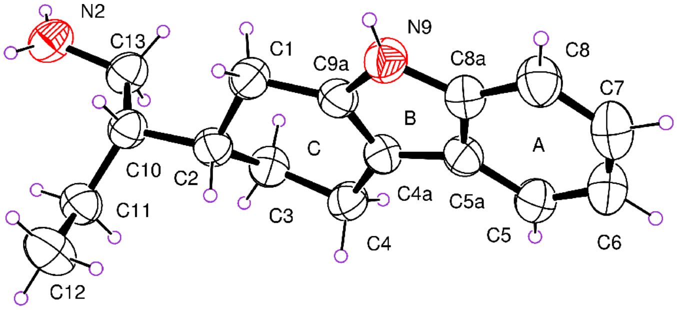


Figure 1
An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

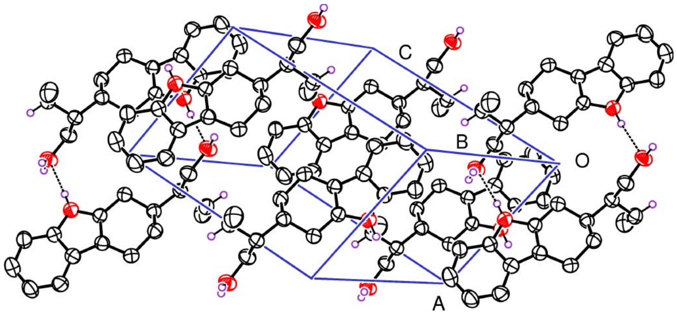


Figure 2
The packing diagram for (I). Hydrogen bonds are shown as dotted lines and H atoms not involved in hydrogen bonding have been omitted.

Compound (I) (Fig. 1) contains a carbazole skeleton with a butylamine side chain bonded as substituent at position 2. As can be seen from the packing diagram (Fig. 2), there are intermolecular hydrogen bonding and intermolecular contacts between the indole N—H group and side-chain NH_2 groups of the neighbouring molecules [$N2^{i}\cdots H9(N9)$ 2.096 Å, $N9—H9\cdots N2^{i}$ 172.1° and $N9^{i}\cdots H2A$ 2.626 Å, $N2—H2A\cdots N9^{i}$ 103.6°, respectively; symmetry code: (i) $-x$, $-y$, $-z+2$]. These intermolecular hydrogen bonding and contacts cause dimerization of the substituted carbazole molecules. Dipole–dipole and van der Waals interactions are also effective in the molecular packing. The substituent and the intermolecular interactions may cause increases in the exocyclic and endocyclic angles C4—C4*A*—C5a [130.8 (2)°], C5—C5a—C4a [135.1 (2)°], C2—C3—C4 [112.2 (2)°] and C1—C9a—C4a [126.4 (2)°].

The absence of any protecting group at atom N9 causes shortening of the C—N bonds [N9—C8a 1.373 (3) Å and N9—C9a 1.382 (3) Å]. They are shorter than the corresponding values [1.390 (10) and 1.404 (9) Å] in *N*-(2-methoxyethyl)-*N*-(2,3,4,9-tetrahydrospiro[1*H*-carbazole-1,2-(1,3)dithiolane]-4-yl)benzenesulfonamide, (VIII) (Patır *et al.*, 1997) and [1.423 (5) and 1.412 (5) Å] in 2,3-dihydro-9-(phenylsulfonyl)-carbazole-4-(1*H*)-one, (IX) (Hökelek *et al.*, 1994). On the other hand, N9—C8a is nearly the same as, but N9—C9a is longer than the corresponding values [1.382 (2) and 1.355 (3) Å] in spiro[carbazole-1(2*H*),2′-[1,3]-dithiolan]-4(3*H*)-one, (X) (Hökelek *et al.*, 1998), while N9—C8a is shorter and N9—C9a is nearly the same with respect to the corresponding ones [1.396 (2) and 1.377 (2) Å] in 9-acetonyl-3-ethylidene-1,2,3,4-tetrahydrospiro[carbazole-1,2′-[1,3]dithiolan]- 4-one, (XI) (Hökelek *et al.*, 1999).

The butylamine side chain in (I) causes notable changes in the geometry of the carbazole core, compared with the reported values in compounds (VI), (VII), (IX), (X) and (XI) (Table 2).

In conclusion, the types of substituent groups, depending on their electron releasing/donating properties, and their bonding positions have a significant effect on the geometry of the carbazole core.

An examination of the deviations from the least-squares planes through the individual rings shows that rings *A* (C5a/C5–C8/C8a) and *B* (C4a/C5a/C8a/N9/C9a) are nearly planar and ring *C* (C1–C4/C4a/C9a) is not planar, with a maximum deviation for the C3 [0.340 (3) Å] atom. These rings are also twisted with respect to each other. The dihedral angles between the best least-squares planes are *A*/*B* = 1.63 (8), *A*/*C* = 8.21 (7) and *B*/*C* = 6.84 (8)°. In ring *C*, the puckering parameters, *i.e.* the angles between the best planes C1/C3/C4/C9a, C4/C4a/C9a and C1/C2/C3, are 7.0 (2) and 50.6 (2)°, respectively. Ring *C* has a sofa conformation with a local pseudo-twofold axis running along the midpoints of the C2—C3 and C4a—C9a bonds.

Experimental

2-(1,2,3,4-Tetrahydrocarbazole-2-yl)butyronitrile (5.0 g, 21.0 mmol) was added slowly to a suspension of lithium aluminium hydride (2.4 g, 62.0 mmol) in tetrahydrofuran (50 ml) at 273 K. The reaction mixture was refluxed for 5 h under a nitrogen atmosphere, then excess of lithium aluminium hydride was destroyed with methanol–water mixture (20:1) and extracted with ethyl acetate. The organic layer was dried with magnesium sulfate and the solvent was evaporated at reduced pressure. The residue was purified by column chromatography using silica gel, ethyl acetate–methanol (9:1) to afford 4.5 g (88%) of the product. The product was recrystallized from an ethyl acetate–cyclohexane mixture (m.p. 425 K).

Crystal data

$C_{16}H_{22}N_2$
$M_r = 242.36$
Triclinic, $P\bar{1}$
$a = 7.9665\ (10)$ Å
$b = 8.911\ (10)$ Å
$c = 10.7318\ (10)$ Å
$\alpha = 69.59\ (6)°$
$\beta = 75.783\ (10)°$
$\gamma = 80.87\ (8)°$
$V = 689.9\ (8)$ Å^3
$Z = 2$
$D_x = 1.167$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 21$–$43°$
$\mu = 0.52$ mm^{-1}
$T = 296\ (2)$ K
Rod, yellow
0.30 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{\min} = 0.855$, $T_{\max} = 0.901$
2927 measured reflections
2807 independent reflections
1637 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 74.2°$
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 11$
$l = -12 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.157$
$S = 1.04$
2406 reflections
163 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0911P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C13—N2	1.463 (3)	C5a—C5	1.408 (3)
N9—C8a	1.373 (3)	C5a—C4a	1.430 (3)
N9—C9a	1.382 (3)	C4a—C4	1.495 (3)
C9a—C4a	1.356 (3)	C1—C2	1.529 (3)
C9a—C1	1.493 (3)	C5—C6	1.371 (3)
C8a—C8	1.385 (3)	C8—C7	1.382 (4)
C8a—C5a	1.411 (3)	C6—C7	1.395 (4)
C4a—C9a—C1	126.41 (19)	C8a—C5a—C4a	106.56 (19)
N9—C9a—C1	123.07 (19)	C9a—C4a—C5a	106.90 (19)
N9—C8a—C8	129.2 (2)	C9a—C4a—C4	122.26 (19)
C8—C8a—C5a	122.5 (2)	C5a—C4a—C4	130.81 (19)
C5—C5a—C8a	118.3 (2)	C2—C3—C4	112.18 (18)
C5—C5a—C4a	135.1 (2)	C4a—C4—C3	110.11 (17)
C1—C9a—C4a—C4	1.0 (3)	C4—C3—C2—C1	65.0 (2)
C4a—C9a—C1—C2	17.2 (3)	C9a—C4a—C4—C3	12.7 (3)
C9a—C1—C2—C3	−47.7 (2)	C2—C3—C4—C4a	−45.1 (2)

Table 2
Comparison of the bond angles (°) in the carbazole core of (I) with the corresponding values in the related compounds (VI), (VII), (IX), (X) and (XI).

Angles	(I)	(VI)	(VII)	(IX)	(X)	(XI)
C2—C3—C4	112.2 (2)	109.9 (2)	110.5 (4)	114.6 (5)	114.7 (2)	115.1 (2)
C4—C4a—C5a	130.8 (2)	128.6 (2)	129.9 (4)	130.4 (4)	130.9 (2)	127.5 (2)
C3—C4—C4a	110.1 (2)	109.0 (2)	110.1 (4)	116.5 (4)	115.9 (2)	114.6 (2)
C1—C9a—N9	123.1 (2)	126.7 (2)	125.0 (3)	126.8 (4)	126.4 (2)	127.5 (2)
C4a—C5a—C5	135.1 (2)	134.7 (2)	133.6 (4)	132.2 (4)	134.7 (2)	134.0 (3)
C4—C4a—C9a	122.3 (2)	124.2 (3)	124.0 (4)	121.5 (4)	122.0 (2)	124.5 (2)
N9—C8a—C8	129.2 (2)	129.1 (2)	130.8 (4)	131.0 (4)	129.8 (2)	129.4 (3)

The positions of the H atoms were calculated geometrically at distances of 0.86 (NH and NH_2), 0.93 and 0.98 (CH), 0.96 (CH_3) and 0.97 (CH_2) from the corresponding atoms, and a riding model was used during the refinement process.

Data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

References

Abraham, D. J. (1975). *The Catharanthus Alkaloids*, edited by W. I. Taylor & N. R. Farnsworth, ch. 7 and 8. New York: Marcel Decker.

Bosch, J. & Bonjoch, J. (1988). *Studies in Natural Product Chemistry*, edited by A. Rahman. Amsterdam: Elsevier.

Fair, C. K. (1990). *MolEN.* Enraf–Nonius, Delft. The Netherlands.

Hökelek, T., Gündüz, H., Patır, S. & Uludağ, N. (1998). *Acta Cryst.* C**54**, 1297–1299.

Hökelek, T. & Patır, S. (1999). *Acta Cryst.* C**55**, 675–677.

Hökelek, T. & Patır, S. (2000*a*). *Anal. Sci.* **16**, 665–666.

Hökelek, T. & Patır, S. (2000*b*). *Anal. Sci.* **16**, 1365–1366.

Hökelek, T., Patır, S., Ergün, Y. & Okay, G. (2001). *Acta Cryst.* C**57**, 414–416.

Hökelek, T., Patır, S., Gülce, A. & Okay, G. (1994). *Acta Cryst.* C**50**, 450–453.

Hökelek, T., Patır, S. & Seferoğlu, Z. (2000). *Anal. Sci.* **16**, 1367–1368.

Hökelek, T., Patır, S. & Uludağ, N. (1999). *Acta Cryst.* C**55**, 114–116.

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

Magnus, P., Sear, N. L., Kim, C. S. & Vicker, N. (1992). *J. Org. Chem.* **57**, 70–78.

Patır, S., Okay, G., Gülce, A., Salih, B. & Hökelek, T. (1997). *J. Heterocycl. Chem.* **34**, 1239–1242.

Phillipson, J. D. & Zenk, M. H. (1980). Editors. *Indole and Biogenetically Related Alkaloids*, ch 3. New York: Academic Press.

Saxton, J. E. (1983). Editor. *Heterocyclic Compounds*, Vol. 25, *The Monoterpenoid Indole Alkaloids*, ch. 8 and 11. New York: Wiley.

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

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