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10,11-Dihydrocarbamazepine (form III)

Charlotte K. Leech,[a] Alastair J. Florence,[b]* Kenneth Shankland,[a] Norman Shankland[b] and Andrea Johnston[b]

[a]ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, England, and [b]Solid-State Research Group, Strathclyde Institute of Pharmacy and Biomedical Sciences, University of Strathclyde, 27 Taylor Street, Glasgow G4 0NR, Scotland

Correspondence e-mail: alastair.florence@strath.ac.uk

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.041
wR factor = 0.101
Data-to-parameter ratio = 12.6

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

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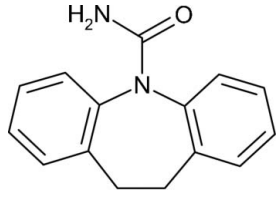
The title compound (systematic name: 10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine-5-carboxamide), $C_{15}H_{14}N_2O$, is shown to crystallize as a triclinic polymorph with $Z' = 2$. N—H···O and N—H···π interactions combine to create a catemeric motif. The robustness of this motif is reflected in the fact that it is also observed in the previously published monoclinic and orthorhombic forms of the compound.

Comment

Dihydrocarbamazepine (DHC), (I), is a recognized impurity in carbamazepine, a dibenzazepine drug used to control seizures (Cyr *et al.*, 1987). DHC is known to crystallize in three polymorphic forms: monoclinic form I [$P2_1/c$; a = 5.505 (1) Å, b = 9.158 (2) Å, c = 24.266 (7) Å, β = 95.95 (2)° at T = 294 K; Bandoli *et al.*, 1992], orthorhombic form II [*Pbca*; a = 9.0592 (4) Å, b = 10.3156 (5) Å, c = 25.0534 (12) Å at T = 120 K; Harrison *et al.*, 2006] and triclinic form III (present work). It also forms a 1:1 solvate with acetic acid (Johnston *et al.*, 2006). The work reported here forms part of a wider investigation that couples automated parallel crystallization (Florence, Johnston, Fernandes *et al.*, 2006) with crystal structure prediction methodology to investigate the basic science underlying the solid-state diversity of carbamazepine and its analogues (Florence, Johnston, Price *et al.*, 2006).



(I)

There are two independent molecules in DHC form III (Fig. 1). The intermolecular interactions combine to create the catemeric motif shown in Fig. 2, with the geometric parameters listed in Table 1. Infinite [0$\bar{1}$0] chains of DHC molecules are linked by hydrogen bonds N4—H4*B*···O1 and N2—H2*B*···O2^{i} [symmetry code: (i) x, $y-1$, z], supplemented by N—H···π interactions, N2—H2*A*···*Cg*4 and N4—H4*A*···*Cg*2^{ii} [symmetry code: (ii) x, $y+1$, z], where *Cg*4 is the centroid of ring *R*4 (C29–C34) and *Cg*2 is the centroid of ring *R*2 (C9–C14). The robustness of this motif is reflected in the fact that it is observed in DHC form II [Fig. 2 of Harrison *et al.* (2006)], DHC form I [Fig. 3 of Bandoli *et al.* (1992)] and in a predicted carbamazepine crystal structure that is isostructural with DHC form II [Fig. 2 of Florence, Leech *et al.* (2006)]. This

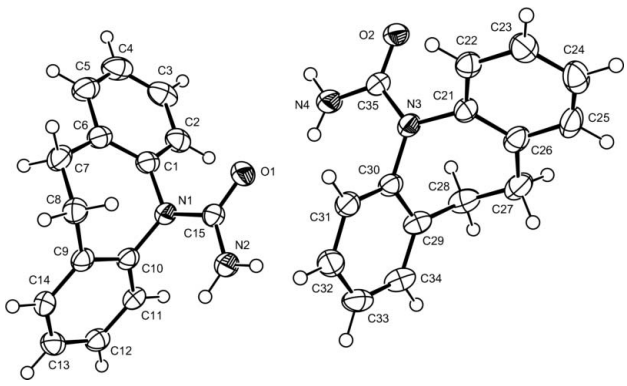


Figure 1
The asymmetric unit of DHC form III with 50% probability displacement ellipsoids.

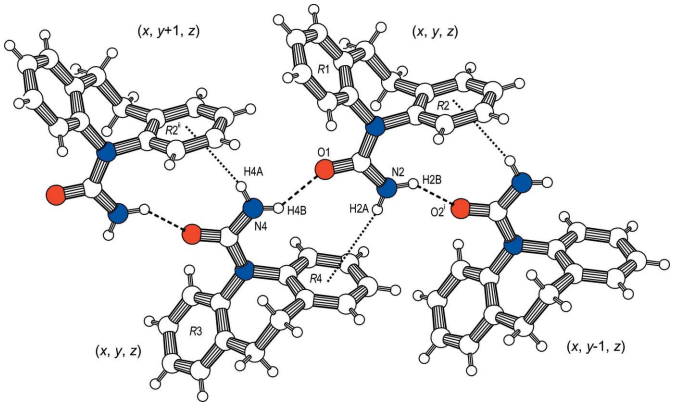


Figure 2
The DHC catemer in form III. Dashed and dotted lines indicate N—H···O and N—H···π interactions, respectively.

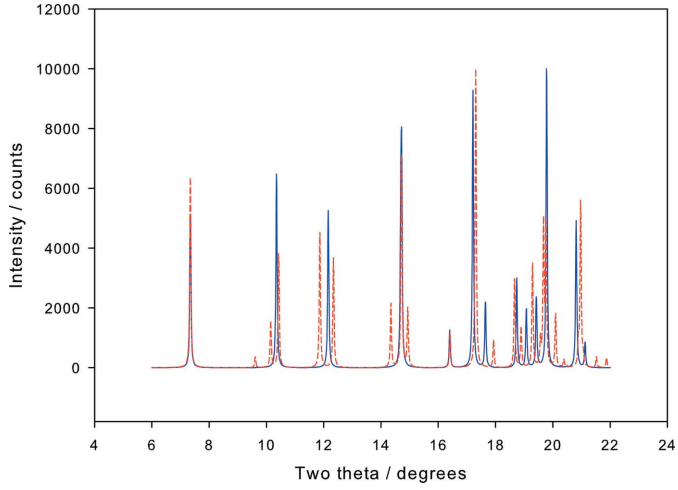


Figure 3
Calculated powder diffraction patterns (λ = 1.54 Å) for DHC form I (blue solid line) and form III (red dashed line).

motif is also observed in the crystal structure of cyheptamide (Leech *et al.*, 2007), an analogue of DHC.

The structures of DHC forms I and III are closely related, but certainly distinct, and there is no evidence of missing symmetry in the form III structure [using the *ADDSYM* algorithm in *PLATON* (Spek, 2003)]. Powder patterns calculated from single-crystal structures offer an effective means of distinguishing polymorphs (Karami *et al.*, 2006) and, in this case, the calculated patterns are quite different, reflecting the small but significant differences in both the lattice parameters and the atomic positions (Fig. 3).

Experimental

DHC was recrystallized from methanol solution by slow evaporation at room temperature to yield single crystals of form I (blocks), form II (hexagonal plates) and form III (needles).

Crystal data

$C_{15}H_{14}N_2O$
M_r = 238.28
Triclinic, $P\overline{1}$
a = 5.4233 (12) Å
b = 9.200 (5) Å
c = 24.189 (6) Å
α = 87.59 (3)°
β = 84.23 (2)°
γ = 88.93 (3)°
V = 1199.6 (8) Å^3
Z = 4
D_x = 1.319 Mg m^{-3}
Cu $K\alpha$ radiation
μ = 0.67 mm^{-1}
T = 150 (2) K
Needle, colourless
0.22 × 0.07 × 0.07 mm

Data collection

Oxford Diffraction Gemini diffractometer
ω and φ scans
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.867, T_{max} = 0.955
12410 measured reflections
4297 independent reflections
2327 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 67.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.101
S = 0.84
4297 reflections
341 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2B···O2^{i}	0.92 (2)	2.02 (3)	2.800 (3)	142.7 (19)
N4—H4B···O1	0.86 (2)	2.11 (3)	2.801 (3)	137.4 (19)
N2—H2A···Cg4	0.89 (3)	3.01 (3)	3.862 (3)	162 (2)
N4—H4A···Cg2^{ii}	0.90 (3)	2.89 (3)	3.765 (3)	166 (2)

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

The amide H atoms were located in difference maps and their coordinates and U_{iso} parameters refined freely. All other H atoms were constrained to geometrically sensible positions in a riding model, with C—H = 0.95–0.99 Å and with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduc-

tion: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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