Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Carbamazepine *N*,*N*-dimethylformamide solvate

Andrea Johnston,[a] Alastair J. Florence[a]* and Alan R. Kennedy[b]

[a]Department of Pharmaceutical Sciences, University of Strathclyde, 27 Taylor Street, Glasgow G4 0NR, Scotland, and [b]Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland

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

Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
R factor = 0.048
wR factor = 0.117
Data-to-parameter ratio = 15.1

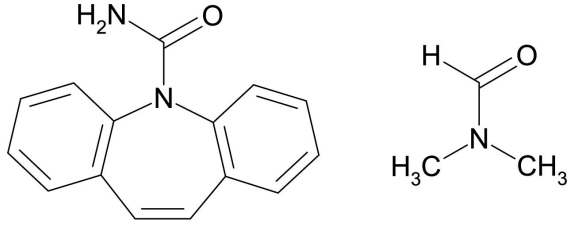
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 6 April 2005
Accepted 20 April 2005
Online 30 April 2005

In the title compound, $C_{15}H_{12}N_2O\cdot C_3H_7NO$, carbamazepine molecules form the $R_2^2(8)$ N—H···O hydrogen-bonded dimer arrangement observed in the crystal structures of each of the four known anhydrous polymorphs. The molecules of *N*,*N*-dimethylformamide are located between adjacent carbamazepine dimers and form an N—H···O hydrogen bond to the *anti*-oriented NH group of the carboxamide moiety of carbamazepine.

Comment

The antiepileptic compound carbamazepine (CBZ) is known to crystallize in at least four anhydrous polymorphic forms (Grzesiak *et al.*, 2003) and the crystal structures of several solvates and co-crystals have also been reported (Fleischman *et al.*, 2003). The title solvate, (I), was produced during an automated parallel crystallization polymorph screen on CBZ. The sample was identified as a new form using multi-sample X-ray powder diffraction analysis of all recrystallized samples (Florence *et al.*, 2003). Subsequent manual recrystallization from a saturated *N*,*N*-dimethylformamide (DMF) solution by slow evaporation at 278 K yielded samples suitable for single-crystal X-ray analysis (Fig. 1).



(I)

In the crystal structure of (I), CBZ molecules form the centrosymmetric hydrogen-bonded $R_2^2(8)$ dimer motif observed in all of the known polymorphs and the majority of CBZ solvate crystal structures (Fleischman *et al.*, 2003) (Fig. 2). CBZ also forms a second N—H···O contact to atom O2 of the solvent molecule. Two C—H···O contacts exist between the DMF methyl H atoms (H17*C* and H18*B*) and atom O1 of CBZ. Atom O2 of DMF is further involved in a third C—H···O contact with an adjacent DMF molecule, forming a centrosymmetric $R_2^2(10)$ motif (Fig. 2). The CBZ dimers pack back-to-back, forming offset face-to-face hydrophobic interactions between adjacent azepine ring systems (Fig. 3).

Experimental

A single-crystal sample of the title compound was recrystallized from DMF solution by slow evaporation at 278 K.

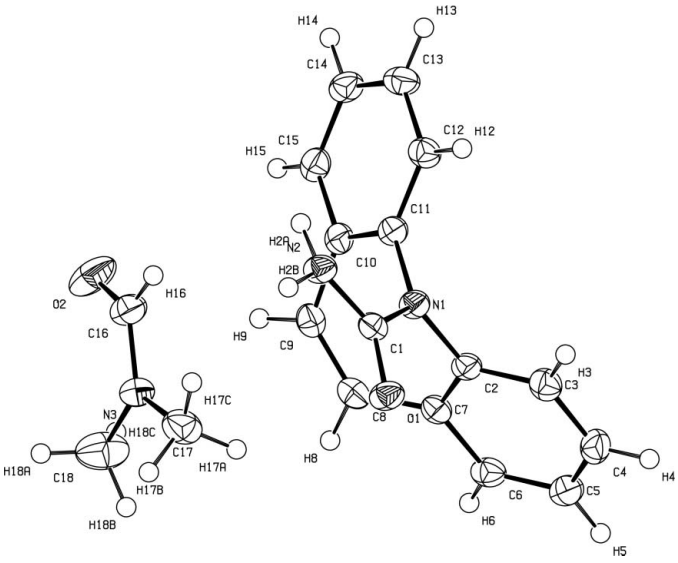


Figure 1
The molecular structure of (I), shown with 50% probability displacement ellipsoids.

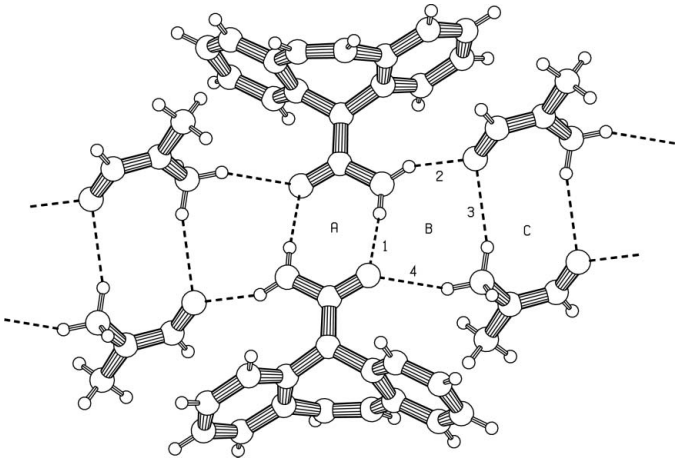


Figure 2
Packing diagram illustrating the non-covalent intermolecular network formed by (1) N2—H2*B*···O1 [N2···O1 = 2.9719 (19)Å O1 in the molecule at $2-x$, $-y$, $1-z$]; (2) N2—H2*A*···O2 [N2···O2 = 2.822 (2) Å; O2 in the molecule at $2-x$, $1-y$, $1-z$]; (3) C18—H18*C*···O2 [C18···O = 3.435 (3) Å; C18 in the molecule at $1+x$, *y*, *z*]; (4) C18—H18*B*···O1 [C18···O1 = 3.259 (2) Å; O1 in the molecule at $2-x$, $-y$, $1-z$] [calculated and illustrated using *PLATON* (Spek, 2003), program version 280604]. These interactions combine to produce three ring motifs: (A) the $R_2^2(8)$ CBZ dimer; (B) an $R_4^4(8)$ motif between CBZ dimers and molecules of DMF and (C) an $R_2^2(10)$ motif connecting DMF molecules in a centrosymmetric dimer configuration.

Crystal data

$C_{15}H_{12}N_2O{\cdot}C_3H_7NO$	$Z = 2$
$M_r = 309.36$	$D_x = 1.305$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 7.7118$ (4) Å	Cell parameters from 3432 reflections
$b = 9.1503$ (4) Å	$\theta = 2.9$–$27.0°$
$c = 11.6969$ (6) Å	$\mu = 0.09$ mm^{-1}
$\alpha = 100.192$ (3)°	$T = 123$ (2) K
$\beta = 95.379$ (2)°	Fragment, colourless
$\gamma = 101.908$ (3)°	0.20 × 0.20 × 0.05 mm
$V = 787.58$ (7) Å^3	

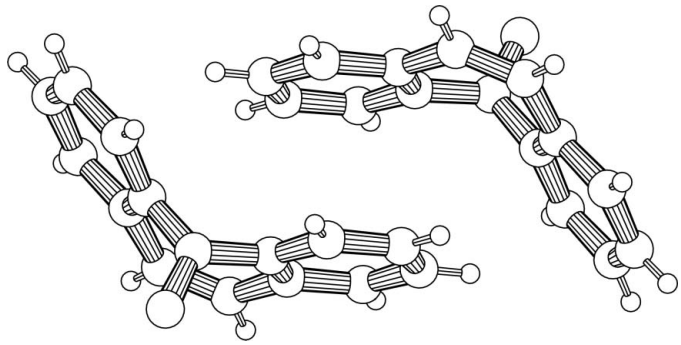


Figure 3
Hydrophobic packing interactions between nearest neighbour CBZ molecules with a centroid–centroid distance of 3.801 (1) Å (the carboxamide groups have been omitted for clarity).

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.054$
ω and φ scans	$\theta_{max} = 27.2°$
Absorption correction: none	$h = -9 \rightarrow 9$
15107 measured reflections	$k = -11 \rightarrow 11$
3476 independent reflections	$l = -14 \rightarrow 14$
2475 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.208P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$(\Delta/\sigma)_{max} = 0.002$
$wR(F^2) = 0.117$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -0.21$ e Å^{-3}
3476 reflections	
230 parameters	
H atoms treated by a mixture of independent and constrained refinement	

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*A*···O2^{i}	0.921 (18)	1.963 (19)	2.822 (2)	154.5 (18)
N2—H2*B*···O1^{ii}	0.884 (19)	2.103 (19)	2.9719 (19)	167.4 (15)
C17—H17*C*···O1^{ii}	0.98	2.51	3.373 (3)	147
C18—H18*B*···O1^{iii}	0.98	2.43	3.259 (2)	142
C18—H18*C*···O2^{iv}	0.98	2.49	3.435 (3)	163

Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $2-x, -y, 1-z$; (iii) $1-x, -y, 1-z$; (iv) $1-x, 1-y, 1-z$.

Five H atoms (H2*A*, H2*B*, H8, H9 and H16) were located in difference maps and refined isotropically, but all other H atoms were constrained to idealized geometry using a riding model; for CH_3 groups, $U_{iso}(H) = 1.5U_{eq}(C)$ and C—H = 0.98 Å, while for CH groups, $U_{iso}(H) = 1.2U_{eq}(C)$ and C—H = 0.95 Å.

Data collection: *COLLECT* (Hooft, 1988) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*; 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*.

We thank the Basic Technology programme of The Research Councils for funding this work under the project Control and Prediction of the Organic Solid State (URL: www.cposs.org.uk).

References

Fleischman, S. G., Kuduva, S. S., McMahon, J. A., Moulton, B., Bailey Walsh, R. D., Rodríguez-Hornedo, N. & Zaworotko, M. J. (2003). *Cryst. Growth Des*. **3**, 909–919.

Florence, A. J., Baumgartner, B., Weston, C., Shankland, N., Kennedy, A. R., Shankland, K. & David, W. I. F. (2003). *J. Pharm. Sci.* **92**, 1930–1938.

Grzesiak, A. L., Lang, M., Kim, K. & Matzger, A. J. (2003). *J. Pharm. Sci.* **92**, 2260–2271.

Hooft, R. (1988). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.