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5-Chlorocarbonyl-10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine

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In the title compound, $C_{15}H_{12}ClNO$, the central seven-membered azepine ring adopts a bent conformation, intermediate between the boat and chair forms. The overall structure of the molecule is similar to a butterfly shape, which is commonly observed for carbamazepine analogues. The planes through the benzene rings on either side of the azepine ring intersect at an angle of 59.0 (1)°. The molecular assembly is primarily stabilized by aromatic π–π interactions.

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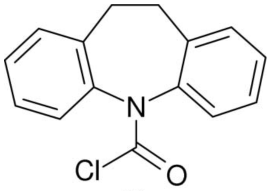
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.063
wR factor = 0.119
Data-to-parameter ratio = 17.7

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

Comment

Carbamazepine and its analogues, which belong to the family of iminostilbenes, have been widely used therapeutically as anticonvulsant agents (Pearce *et al.*, 2002; Czapinski *et al.*, 2005). In order to study the structure–activity relationships of these compounds, numerous structures of iminostilbene derivatives have been reported (Lisgarten *et al.*, 1989; Lang *et al.*, 2002; Hempel *et al.*, 2005; Nagaraj *et al.*, 2005; Johnston *et al.*, 2005). The crystal structure analysis of the title compound, (I), reported here was undertaken as a part of an ongoing programme of structural studies of molecules of pharmaceutical interest.



(I)

The molecular structure and conformation of (I) are shown in Fig. 1. The planes of atoms N5/C1–C4/C11–C13 and N5/C6–C9/C10/C11/C14/C15 intersect at an angle of 59.0 (1)°. The central seven-membered azepine ring (N5/C10–C15) adopts a bent conformation with five coplanar atoms (N5/C10/C11/C14/C15) (Bocian *et al.*, 1975; Bocian & Strauss, 1977). Six distinct conformations have been identified and characterized for a classical cycloheptane ring: (i) boat, (ii) chair, (iii) twist–boat, (iv) twist–chair, and the two high-energy intermediate transition states, namely, (v) bent transition state between the first two and, (vi) twisted transition state between the latter two (Hendrickson, 1961, 1967; Bocian *et al.*, 1975; Bocian & Strauss, 1977). The bent transition state of the seven-membered ring with five coplanar atoms is one of the most popular conformation among carbamazepine analogues, which has been improperly referred as twist–boat or half-boat by many authors. In addition to the puckering parameters of the ring described in the literature (Bocian *et al.*, 1975; Bocian & Strauss, 1977), the 'twist' nomenclature in its classical sense mean the form with C_2 (axial) symmetry (Hendrickson, 1961, 1967), while the present conformation of the ring possesses C_s (mirror plane) symmetry.The puckering parameters (Cremer & Pople, 1975) of the azepine ring are, q_2 = 0.813 (3) Å, q_3 = 0.284 (3) Å, φ_2 = 202.9 (2)° and φ_3 = 125.4 (7)°, and the total puckering amplitude Q_T = 0.861 (3) Å. The internal torsion angles of the azepine ring are indicated in Fig. 1. The bent conformation of the seven-membered ring possesses a mirror symmetry about the plane passing through atom C15 and bisecting the C12—C13 bond. The asymmetry parameter (Duax *et al.*, 1976), $\Delta C_s(m)$, is 8.2°. Due to the present conformation of the azepine ring, the molecule assumes a butterfly shape, as previously observed (Hempel *et al.*, 2005; Nagaraj *et al.*, 2005).

In the absence of any potential hydrogen-bond donors, the crystal packing of (I) is mainly stabilized by aromatic π–π interactions of the edge-to-face type, in addition to van der Waals forces (Fig. 2). The geometric parameters, *i.e.* centroid···centroid separations, interplanar angles and minimal C—C separations in the π–π interactions, respectively, are as follows $Cg1\cdots Cg1(2-x, 2-y, -\frac{1}{2}+z)$ = 4.926 (2) Å, 32.3°, 3.46 Å; $Cg1\cdots Cg2(2-x, 1-y, \frac{1}{2}+z)$ = 5.057 (2) Å, 79.0°, 3.60 Å; $Cg2\cdots Cg2(\frac{3}{2}-x, y, -\frac{1}{2}+z)$ = 4.987 (2) Å, 70.5°, 3.76 Å. *Cg*1 and *Cg*2 are the centroids of ring 1 (atoms C1–C4/C12/C13) and ring 2 (atoms C6–C9/C14/C15), respectively.

Experimental

The title compound (Jubilant Organosys, Nanjangaud, India) was crystallized from ethyl methyl ketone.

Crystal data

$C_{15}H_{12}ClNO$
M_r = 257.71
Orthorhombic, $Pca2_1$
a = 16.654 (3) Å
b = 10.646 (2) Å
c = 7.2599 (14) Å
V = 1287.1 (4) Å^3
Z = 4
D_x = 1.330 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 870 reflections
θ = 5–27°
μ = 0.28 mm^{-1}
T = 295 (2) K
Plate, colourless
0.58 × 0.20 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.926, T_{max} = 0.971
6801 measured reflections

2890 independent reflections
2159 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 27.9°
$h = -18 \rightarrow 21$
$k = -14 \rightarrow 11$
$l = -9 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.119
S = 1.13
2890 reflections
163 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.0447P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Absolute structure: Flack (1983), with 1414 Friedel pairs
Flack parameter: 0.03 (10)

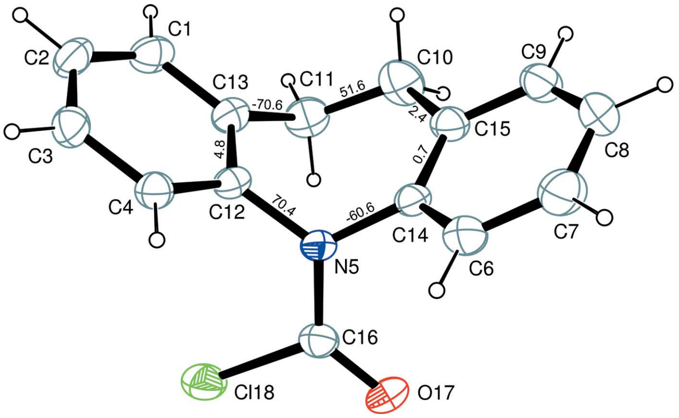


Figure 1
A view of molecule (I). The numerical figures refer to the internal torsion angles (°) of the central azepine ring in a bent conformation; s.u. values are in the range 0.4–0.5°. Displacement ellipsoids are drawn at the 30% probability level. H atoms are shown as small spheres of arbitrary radii.

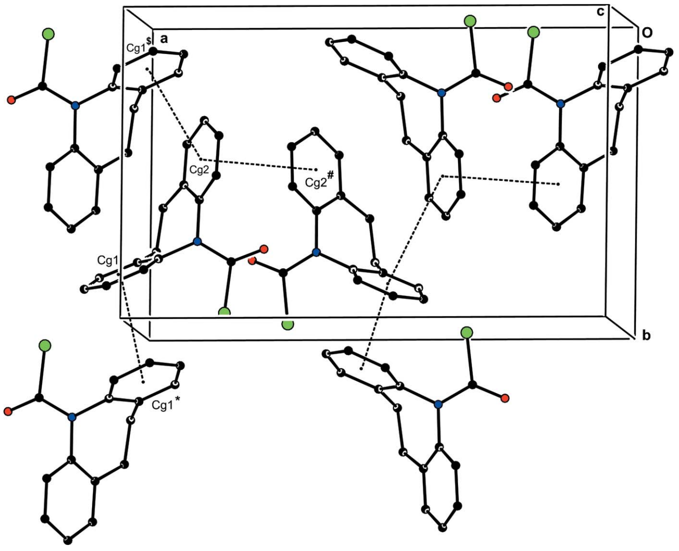


Figure 2
The crystal packing of (I), stabilized by π–π interactions. *Cg*1 and *Cg*2 are the centroids of ring 1 and ring 2, respectively. Atoms labelled with an asterisk (*), dollar sign ($) or hash (#) are at the symmetry positions $(2-x, 2-y, -\frac{1}{2}+z)$, $(2-x, 1-y, -\frac{1}{2}+z)$ and $(\frac{3}{2}-x, y, -\frac{1}{2}+z)$, respectively. Colour key: C black, H white, Cl green, N blue, O red.

All H atoms were positioned geometrically and refined as riding on their parent atoms, with C_{ar}—H = 0.93 Å and methylene C—H = 0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

Thanks are expressed to Jubilant Organosys for providing the sample of (I) for this structural study. We are grateful to Professor T. N. Guru Row, who provided access to the CCD facility, set up under the IRHPA-DST Programme.

Acta Cryst. (2005). E**61**, o3718–o3720 Vijay *et al.* • $C_{15}H_{12}ClNO$ **o3719**

References

Bocian, D. F., Pickett, H. M., Rounds, T. C. & Strauss, H. L. (1975). *J. Am. Chem. Soc.* **97**, 687–695.

Bocian, D. F. & Strauss, H. L. (1977). *J. Am. Chem. Soc.* **99**, 2876–2882.

Bruker (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2001). *SMART* (Version 5.628) and *SAINT-Plus* (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Czapinski, P., Blaszczyk, B. & Czuczwar, S. J. (2005). *Curr. Top. Med. Chem.* **5**, 3–14.

Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by E. L. Eliel & N. Allinger, pp. 271–383. New York: John Wiley.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Hempel, A., Camerman, N., Camerman, A. & Mastropaolo, D. (2005). *Acta Cryst.* E**61**, o1313–1315.

Hendrickson, J. B. (1961). *J. Am. Chem. Soc.* **83**, 4537–4547.

Hendrickson, J. B. (1967). *J. Am. Chem. Soc.* **89**, 7047–7061.

Johnston, A., Florence, A. J. & Kennedy, A. R. (2005). *Acta Cryst.* E**61**, o1777–1779.

Lang, M., Kampf, J. W. & Matzger, A. J. (2002). *J. Pharm. Sci.* **91**, 1186–1190.

Lisgarten, J. N., Palmer, R. A. & Saldanha, J. W. (1989). *Acta Cryst.* C**45**, 656–658.

Nagaraj, B., Yathirajan, H. S. & Lynch, D. (2005). *Acta Cryst.* E**61**, o1609–1610.

Pearce, R. E., Vakkalagadda, G. R. & Steven Leeder, J. (2002). *Drug Metab. Dispos.* **30**, 1170–1179.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

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

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

o3720 Vijay *et al.* • $C_{15}H_{12}ClNO$ *Acta Cryst.* (2005). E**61**, o3718–o3720