

5-Chlorocarbonyl-10,11-dihydro-5H-dibenz[*b,f*]azepineT. Vijay,^a H. G. Anilkumar,^b
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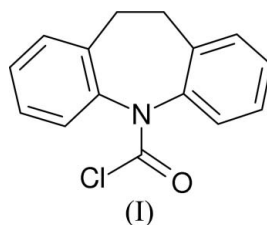
Key indicators

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 = 17.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, C₁₅H₁₂ClNO, 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.

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.



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 to 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

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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, $\varphi_2 = 202.9$ (2)° and $\varphi_3 = 125.4$ (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. $Cg1$ and $Cg2$ 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) Å³
 $Z = 4$
 $D_x = 1.330$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 870 reflections
 $\theta = 5$ –27°
 $\mu = 0.28$ 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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 27.9^\circ$
 $h = -18 \rightarrow 21$
 $k = -14 \rightarrow 11$
 $l = -9 \rightarrow 8$

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

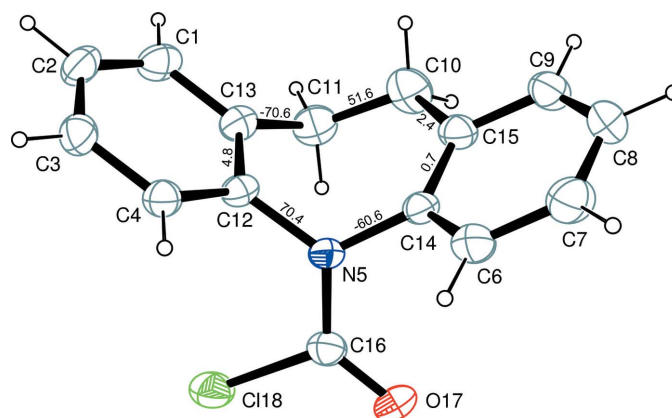


Figure 1

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.

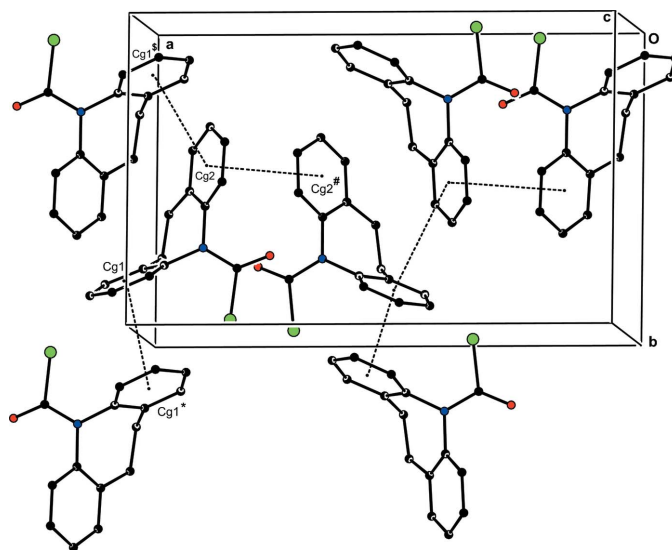


Figure 2

The crystal packing of (I), stabilized by π – π interactions. $Cg1$ and $Cg2$ 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 $C_{\text{ar}}\text{--H} = 0.93$ Å and methylene $C\text{--H} = 0.97$ Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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.

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