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2,3-Dihydro-2,2-dimethylbenzofuran-7-yl *N*-methylcarbamate

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.005 Å
R factor = 0.041
wR factor = 0.108
Data-to-parameter ratio = 9.1

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, $C_{12}H_{15}NO_3$, crystallizes with two independent molecules in the asymmetric unit. The bond lengths and angles in both molecules are within normal ranges. There are some weak intermolecular hydrogen-bond interactions in the crystal structure, which provide stabilization.

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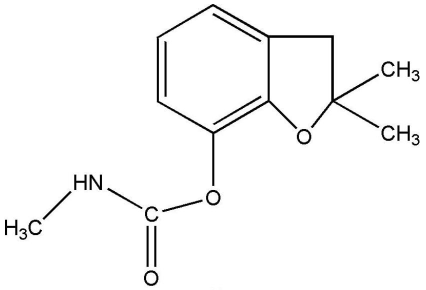
Comment

The title compound, (I), trade name Carbofuran, is a popular systemic carbamate insecticide that is utilized worldwide with a broad spectrum of activity (Tomlin, 1994; Edward, 1967). It is extensively used for the control of all types of stem borers in rice and sugar cane, rice BPH, and fruit and stem borers in vegetables. It also has excellent nematicide properties. In addition, Carbofuran is an inhibitor of acetylcholinesterase (AchE). In order that the chemical consequences of complex formation between AchE and quaternary inhibitors may be interpreted, it is essential to elucidate the nature of the forces favouring adsorption on the active surface, such as Coulombic attractions, hydrogen bonding, van der Waals forces and hydrophobic interactions (Belleau & Lacasse, 1964). In order to gain further insight into the structural features of (I) that determine biological activity, the single-crystal structure was determined and is reported here.



(I)

Carbofuran crystallizes with two independent molecules in the asymmetric unit (Fig. 1). The bond lengths and angles in both molecules are in agreement with those reported for similar compounds incorporating the 2,3-dihydro-2,2-dimethylbenzofuran group (Kossakowski *et al.*, 2002). The dihedral angle formed by the O5/C21/O6/N2/C22 plane with the hetero-ring plane C13–C20/O4/O5 is 85.12 (3)°. In the second independent molecule, the C5/O2/C9/O3/N1/C10 plane makes a dihedral angle of 79.67 (5)° with the C2–C8/O1 plane. The 2,3-dihydrobenzofuran ring (C13–C20/O4) is essentially planar, whereas the C1–C8/O1 ring system shows significant deviation from planarity, with atom C1 lying 0.142 (2) Å out of the plane of the other eight atoms.

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Weak C—H···O and C—H···N intra- and intermolecular hydrogen-bond interactions stabilize the crystal structure (Table 2).

Experimental

The title compound, (I), was prepared according to the method of Edward (1967). *o*-Bromophenol was converted to *o*-bromophenyl methallyl ether by reaction with methallyl chloride in the presence of an alkali metal hydroxide. *o*-Bromophenyl methallyl ether was then heated, producing 2-bromo-6-methallylphenol or 2-bromo-6-isobutenylphenol, which then cyclized to form the title compound. 2,3-Dihydro-2,2-dimethyl-7-bromobenzofuran (50 g) was mixed with a 7% solution of sodium hydroxide (603 g) in ethylene glycol in a glass flask. Cupric nitrate trihydrate (2.5 g) was added and the apparatus was purged with nitrogen. The mixture was stirred and heated at 453 K for 5 h, and was then heated at 468 K for 3 h. The solution was cooled, diluted with water (1 l) and washed with ether. The aqueous phase was acidified with sulfuric acid and extracted with two 250 ml protions of ether. Evaporation of the solvent from the combined extracts produced pure 2,3-dihydro-2,2-dimethyl-7-benzofuranol in a good yield (90%). Into a 12 l flask were added 2,3-dihydro-2,2-dimethyl-7-benzofuranol (2.3 kg), diethyl ether (3.5 l) and triethylamine (6 g). The solution was cooled to 290 K and methyl isocyanate (839 g) was added over a period of 35 min with external cooling to maintain the temperature below 300 K. After standing overnight, the slurry was filtered, washed with ether and dried to produce white crystalline (I) (yield 78%; m.p. 426–427 K). MS (ESI): *m*/*z* (%): 221 (M^+, 8), 165 (10), 164 (100), 149 (61), 131 (18), 122 (19), 91 (10). Single crystals suitable for X-ray measurements were obtained by recrystallization from ethanol at room temperature.

Crystal data

$C_{12}H_{15}NO_3$
$M_r = 221.25$
Orthorhombic, $P2_12_12_1$
$a = 10.2654 (15)$ Å
$b = 13.515 (2)$ Å
$c = 17.230 (3)$ Å
$V = 2390.5 (6)$ Å^3
$Z = 8$
$D_x = 1.230$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2998 reflections
$\theta = 2.3–21.9°$
$\mu = 0.09$ mm^{-1}
$T = 294 (2)$ K
Block, colourless
0.38 × 0.20 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.956$, $T_{max} = 0.989$
13513 measured reflections

2751 independent reflections
1787 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 26.4°$
$h = -12 \rightarrow 12$
$k = -16 \rightarrow 16$
$l = -9 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.109$
$S = 1.04$
2751 reflections
303 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 0.1511P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

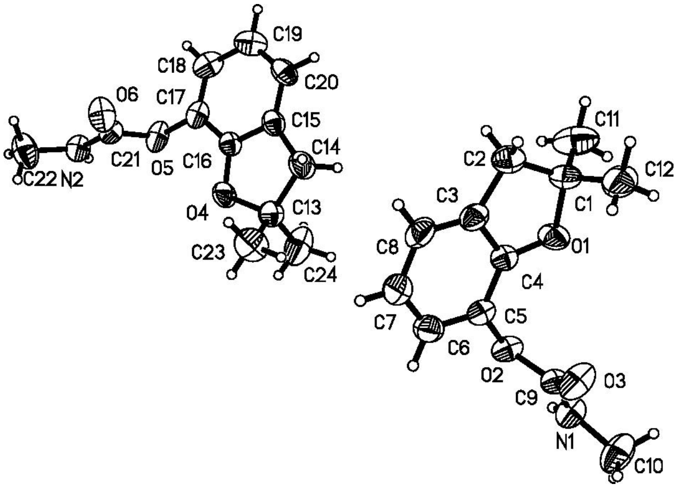

Figure 1
View of the title compound (I), with displacement ellipsoids for non-H atoms drawn at the 40% probability level.

Table 1
Selected geometric parameters (Å, °).

N1—C9	1.324 (4)	N2—C21	1.329 (4)
N1—C10	1.435 (4)	N2—C22	1.439 (4)
O1—C4	1.361 (4)	O4—C16	1.363 (3)
O1—C1	1.491 (4)	O4—C13	1.491 (4)
C9—N1—C10	122.9 (3)	C21—N2—C22	122.7 (3)
C4—O1—C1	107.6 (2)	C16—O4—C13	107.7 (2)
O1—C1—C2	105.4 (3)	O4—C13—C14	105.5 (2)
C3—C2—C1	104.0 (3)	C15—C14—C13	103.6 (3)
C4—O1—C1—C2	−11.7 (3)	C16—O4—C13—C14	9.1 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O6^{i}	0.82 (3)	2.26 (3)	3.020 (4)	153 (3)
N2—H2···O3^{ii}	0.82 (3)	2.17 (3)	2.949 (4)	159 (3)

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

All H atoms bound to C atoms were placed in calculated positions and were constrained to ride on their parent atoms (C—H = 0.93–0.97 Å), with $U_{iso}(H) = 1.2U_{eq}(C)$ for the aryl and methylene H atoms and $1.5U_{eq}(C)$ for the methyl H atoms. The positions and isotropic displacement parameters of the NH H atoms were refined freely. In the absence of significant anomalous dispersion effects, Friedel pairs were averaged.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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