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1-Chloroacetyl-2,4-diphenyl-2,3-dihydro-1*H*-1,5-benzodiazepine

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The title compound, $C_{23}H_{19}ClN_2O$, crystallizes as a racemic mixture having two molecules in the asymmetric unit. The structure is disordered.

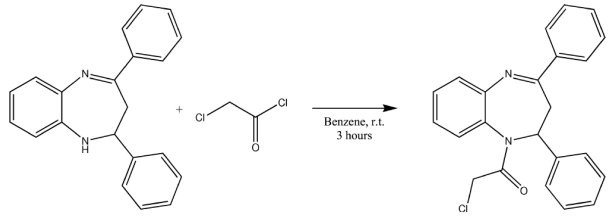
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.007 Å
Disorder in solvent or counterion
R factor = 0.068
wR factor = 0.201
Data-to-parameter ratio = 15.2

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

Comment

Benzodiazepines are an important class of psychotherapeutic compounds. Here we describe the racemic mixture resulting from an *N*-chloroacetylation of the corresponding racemate 2,4-diphenyl-2,3-dihydro-1*H*-1,5-benzodiazepine (Insuasty *et al.*, 1992).



(I)

The structure, (I), is disordered with the minor component consisting of two molecules whose coordinates are related to those of the major component by the transformation (x, $-y$, z). As can be seen in Table 1, the bond distances and angles of the two molecules in the asymmetric unit show no differences at a significance level of 3σ. There are some slight variations in the magnitudes of the torsion angles of the diazepine rings involving atoms Nn6, Cn7 and Cn8 (n = 1 or 2). The two molecules of the asymmetric unit were chosen such that they were linked by the weak C122—H12A···O22 hydrogen bond; for details see Table 2. A similar bond involving C222—H22A···O21(x, $-1+y$, z) links the molecules by a $C_2^2(8)$ chain (Bernstein *et al.*, 1995), running parallel to the b axis (Fig. 2).

The molecules of the R enantiomer are linked together to form a $C9$ chain by the weak hydrogen bond C194—H194···O12(x, $2-y$, $z-\frac{1}{2}$) (Fig. 3). The molecules of the S conformer are linked by an identical chain formed by the weak hydrogen bond C294—H294···O22(x, $1-y$, $z-\frac{1}{2}$) (Table 2). These chains run parallel to the c axis.

Experimental

A solution of 2,4-diphenyl-1,5-benzodiazepine (2.0 mmol) and chloroacetyl chloride (2.0 mmol) in 20 ml of anhydrous benzene was stirred at room temperature for 3 h. After the solvent was removed, the title compound was separated by column chromatography on silica gel, using chloroform as eluent, and obtained as yellow crystals after solvent evaporation (yield 90%, m.p. 449 K), which were suitable for X-ray diffraction. Analysis calculated for $C_{23}H_{19}ClN_2O$: C 73.69, H 5.11, N 7.47%; found: C 73.78, H 5.17, N 7.42%.

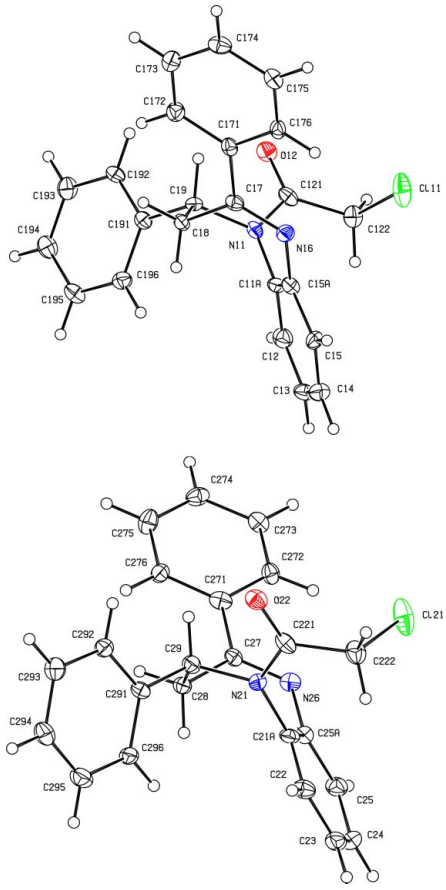


Figure 1
A view of the two molecules in the asymmetric unit of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

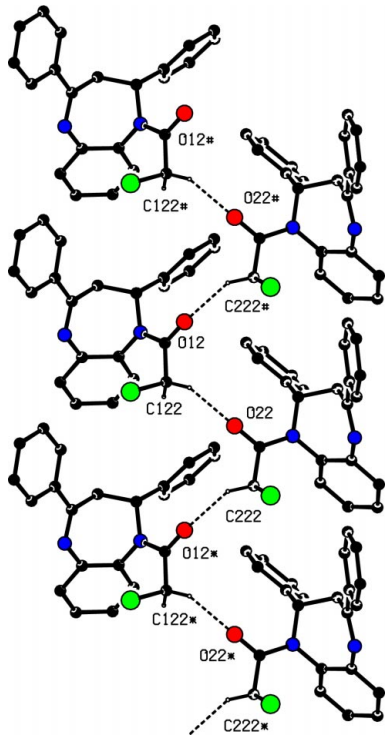


Figure 2
A view of the crystal structure, showing the $C_2^2(8)$ chain which runs parallel to the b axis. All H atoms not involved in hydrogen bonding and the unit-cell outline have been omitted for the sake of clarity. The molecules labelled with an asterisk (*) are at (x, $y-1$, z) and those labelled with a hash (#) are at (x, $y+1$, z).

Crystal data

$C_{23}H_{19}ClN_2O$	D_x = 1.345 Mg m^{-3}
M_r = 374.85	Mo Kα radiation
Monoclinic, Cc	Cell parameters from 7396 reflections
a = 31.7081 (8) Å	θ = 2.9–27.3°
b = 7.8174 (2) Å	μ = 0.22 mm^{-1}
c = 15.4208 (5) Å	T = 120.0 (2) K
β = 104.344 (1)°	Plate, colourless
V = 3703.27 (18) Å^3	0.36 × 0.12 × 0.08 mm
Z = 8	

Data collection

Nonius KappaCCD diffractometer	7396 independent reflections
φ scans and ω scans with κ offsets	5168 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)	R_{int} = 0.095
T_{min} = 0.925, T_{max} = 0.983	θ_{max} = 27.3°
17924 measured reflections	$h = -40 \rightarrow 40$
	$k = -10 \rightarrow 7$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.001
$R[F^2 > 2\sigma(F^2)]$ = 0.069	$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$wR(F^2)$ = 0.201	$\Delta\rho_{min}$ = −0.40 e Å^{-3}
S = 1.04	Extinction correction: *SHELXL97*
7396 reflections	Extinction coefficient: 0.0041 (7)
488 parameters	Absolute structure: Flack (1983), 4142 Friedel pairs
H-atom parameters constrained	Flack parameter = 0.09 (10)
$w = 1/[\sigma^2(F_o^2) + (0.1033P)^2 + 1.4124P]$ where $P = (F_o^2 + 2F_c^2)/3$	

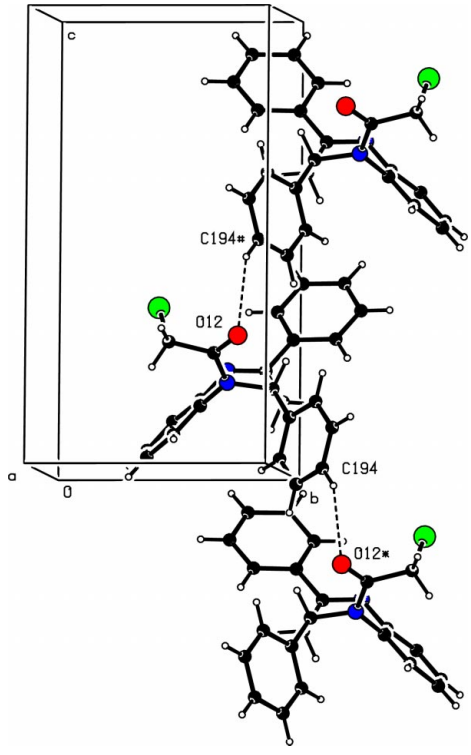


Figure 3
A view of the crystal structure, showing the $C(9)$ chain involving molecules of the R enantiomer which runs parallel to the c axis. A similar chain links molecules of the S enantiomer together. The molecule labelled with an asterisk (*) is at (x, $2-y$, $z-\frac{1}{2}$) and that labelled with a hash (#) is at (x, $2-y$, $z+\frac{1}{2}$).

Table 1
Selected geometric parameters (Å, °).

N11—C11*A*	1.424 (6)	N21—C21*A*	1.436 (6)
N11—C19	1.497 (6)	N21—C29	1.486 (6)
C11*A*—C15*A*	1.393 (7)	C21*A*—C25*A*	1.390 (6)
C15*A*—N16	1.423 (6)	C25*A*—N26	1.423 (6)
N16—C17	1.288 (6)	N26—C27	1.294 (6)
C17—C18	1.521 (7)	C27—C28	1.501 (7)
C18—C19	1.526 (7)	C28—C29	1.531 (7)
C11*A*—N11—C19	119.7 (4)	C21*A*—N21—C29	120.8 (4)
C15*A*—C11*A*—N11	119.5 (4)	C25*A*—C21*A*—N21	119.3 (4)
C11*A*—C15*A*—N16	123.0 (4)	C21*A*—C25*A*—N26	123.2 (4)
C17—N16—C15*A*	118.0 (4)	C27—N26—C25*A*	118.6 (4)
N16—C17—C18	121.4 (4)	N26—C27—C28	121.1 (4)
C17—C18—C19	110.6 (4)	C27—C28—C29	110.7 (4)
N11—C19—C18	108.4 (4)	N21—C29—C28	108.0 (4)
C19—N11—C11*A*—C15*A*	−65.9 (6)	C29—N21—C21*A*—C25*A*	65.1 (6)
N11—C11*A*—C15*A*—N16	−0.6 (7)	N21—C21*A*—C25*A*—N26	0.6 (7)
C11*A*—C15*A*—N16—C17	49.5 (6)	C21*A*—C25*A*—N26—C27	−47.2 (7)
C15*A*—N16—C17—C18	0.7 (6)	C25*A*—N26—C27—C28	−3.4 (7)
N16—C17—C18—C19	−77.7 (5)	N26—C27—C28—C29	79.6 (6)
C17—C18—C19—N11	54.5 (5)	C21*A*—N21—C29—C28	−29.2 (5)
C11*A*—N11—C19—C18	29.4 (5)	C27—C28—C29—N21	−54.9 (5)
N16—C17—C171—C176	−1.8 (6)	C21*A*—N21—C221—O22	−175.4 (4)
C18—C17—C171—C176	179.6 (4)	C29—N21—C221—O22	6.4 (6)
N16—C17—C171—C172	−178.5 (4)	O22—C221—*C*222—Cl21	−99.0 (5)
C18—C17—C171—C172	2.9 (7)	N21—C221—*C*222—Cl21	78.7 (5)
C11*A*—N11—C121—O12	175.7 (4)	N26—C27—C271—C276	175.2 (5)
C19—N11—C121—O12	−7.0 (6)	C28—C27—C271—C276	−4.2 (7)
O12—C121—C122—Cl11	99.1 (5)	N26—C27—C271—C272	−4.3 (7)
N11—C121—C122—Cl11	−79.6 (5)	C28—C27—C271—C272	176.3 (4)
N11—C19—C191—C192	−113.5 (5)	N21—C29—C291—C292	114.4 (5)
C18—C19—C191—C192	121.9 (5)	C28—C29—C291—C292	−122.1 (5)
N11—C19—C191—C196	67.8 (6)	N21—C29—C291—C296	−66.2 (6)
C18—C19—C191—C196	−56.9 (6)	C28—C29—C291—C296	57.4 (6)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C122—H12*A*···O22	0.99	2.23	3.110 (19)	148
*C*222—H22*B*···O12^{i}	0.99	2.26	3.144 (19)	148
C194—H194···O12^{ii}	0.95	2.57	3.297 (16)	133
C294—H294···O22^{iii}	0.95	2.58	3.285 (16)	132

Symmetry codes: (i) $x, y-1, z$; (ii) $x, 2-y, z-\frac{1}{2}$; (iii) $x, 1-y, z-\frac{1}{2}$.

H atoms were treated as riding atoms with aromatic C—H = 0.95 Å, CH_2 C—H = 0.99 Å and CH C—H = 1.00 Å. The structure initially refined to an *R* of 9.55% but the difference map showed several high peaks, the highest two being 1.60 and 1.59 e Å^{-3}. A map of the highest 30 peaks showed two diazepine rings with the attached Cl side chain, the highest peaks, those mentioned above, being the Cl atoms; however, only fragments of the attached phenyl groups could be located. The coordinates of the peaks which could be found indicated that disordered molecules were present with coordinates $x, -y, z$ with respect to those of the major component molecules. Refinement of a group site-occupancy factor for the major component gave a value of 0.92, which is in agreement with the height of the highest peaks in the difference map. By varying the value of the site-occupancy factor around this value after the final refinement it was found that this value lay within the optimal range as far as low *R* factor was concerned and so the refinement was carried out with the fixed values of 0.92 (0.08) for the site-occupancy factors of the major (minor) components. The minor component was created by taking the atoms in the major component, changing the sign of the *y* coordinates and adding a shift of 1 to them to bring the disordered molecules into the unit cell. The displacement parameters of the minor components were isotropic. Attempts at refinement lead to instability, so the minor component was held fixed, with positional and displacement parameters not refined. The process was repeated several times, with the minor component being recalculated after several cycles of least squares. The *R* factor dropped to 6.85%.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

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