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6-Chloro-1-(α-chloroacetyl)-1,2,3,4-tetrahydro-4-methylquinoline-2-spirocyclohexane

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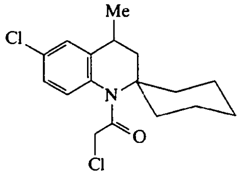
Abstract

In the title compound, $C_{17}H_{21}Cl_2NO$, the heterocyclic part of the molecule has a conformation between twist and screw-boat. The N atom shows considerable sp^2 hybridization. The cyclohexane ring adopts a chair conformation. The molecules in the crystal are held together by van der Waals interactions.

Comment

6-Chloro-1-(α-chloroacetyl)-1,2,3,4-tetrahydro-4-methylquinoline-2-spirocyclohexane is a new *N*-substituted 1,2,3,4-tetrahydrospiro-2-quinoline. Synthetic tetrahydroquinoline derivatives possess high antibacterial, antiarrhythmic and antihypertensive activities (Jones, 1977; Yates, 1984). They also act as potent virucides and analgesics. Compounds containing tricyclic systems, such as the title compound, (I), are useful in the synthesis of alkaloids which have the tetrahydroquinoline moiety (Inubushi & Ibuka, 1977; Kametani *et al.*, 1986; Hill & Raphael, 1986). In order to obtain detailed information on its molecular conformation, we determined the structure of (I) using X-ray techniques.



(I)

A perspective view of (I) showing the atomic numbering scheme is given in Fig. 1. The bond lengths and angles have normal values. The saturated part of the quinoline moiety has a conformation between twist ($^1T_3$) and screw-boat ($^4S_3$). The N atom is sp^2 hybridized: the sum of the three bond angles around the N atom is 359.9°. The aromatic ring is planar within experimental error. The cyclohexane ring at C2 has a chair conformation.

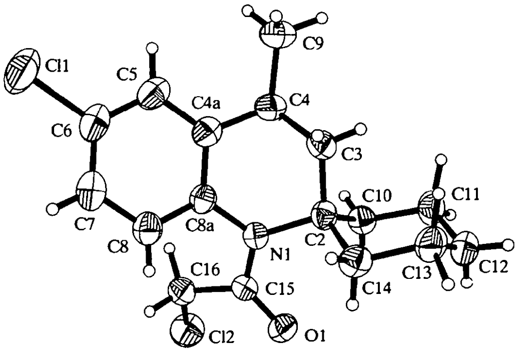


Fig. 1. The molecular structure of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of an arbitrary radius.

The molecules in the crystal are held together by van der Waals forces (Fig. 2). There is one intramolecular C—H···O interaction [C10···O1 2.926 (3) Å] and two intermolecular interactions (Desiraju, 1991), one of type C—H···O [C16···O1^{i} 3.376 (3) Å] and the other of type C—H···Cl [C9···Cl2^{ii} 3.672 (3) Å] [symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x+1, -y+1, -z+1$].

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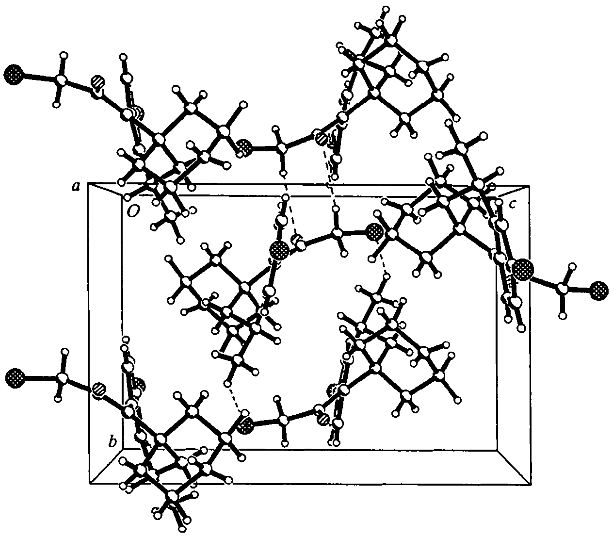

Fig. 2. A perspective drawing of the packing arrangement in (I) along the *a* axis. Dashed lines indicate C—H···O and C—H···Cl intermolecular interactions.

Experimental

The title compound was prepared by heating 6-chlorospirotetrahydroquinoline (2.7 g, 0.011 mol) with chloroacetyl chloride (1.22 g, 0.012 mol) and triethylamine (1.22 g, 0.042 mol) in anhydrous benzene (10 ml) at 318 K for 4 h (Kouznetsov *et al.*, 1991, 1993). The mixture was then treated with Na_2CO_3 solution and extracted with ethanol. The product was recrystallized from *n*-heptane solution by slow evaporation of the solvent at room temperature, to yield colourless crystals of (I) (m.p. 361-363 K).

Crystal data

$C_{17}H_{21}Cl_2NO$
$M_r = 326.25$
Monoclinic
$P2_1/n$
$a = 11.356\,(1)$ Å
$b = 9.843\,(1)$ Å
$c = 14.452\,(2)$ Å
$\beta = 91.56\,(1)^\circ$
$V = 1614.8\,(3)$ Å^3
$Z = 4$
$D_x = 1.342$ Mg m^{-3}
$D_m = 1.32$ Mg m^{-3}
D_m measured by flotation in KI solution and water

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.0\text{–}22.5^\circ$
$\mu = 0.400$ mm^{-1}
$T = 293\,(2)$ K
Cubic
0.24 × 0.23 × 0.23 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
5902 measured reflections
4697 independent reflections
2845 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$

$\theta_{\rm max} = 30^\circ$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 100 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.177$
$S = 1.157$
4693 reflections
275 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.007$

$\Delta\rho_{\rm max} = 0.281$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.309$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0064 (18)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cl1—C6	1.746 (2)	C4a—C5	1.388 (3)
Cl2—C16	1.771 (2)	C4a—C8a	1.402 (3)
N1—C15	1.359 (3)	C5—C6	1.399 (4)
N1—C8a	1.434 (2)	C6—C7	1.374 (4)
N1—C2	1.526 (2)	C7—C8	1.385 (3)
O1—C15	1.220 (2)	C8—C8a	1.391 (3)
C2—C3	1.528 (3)	C10—C11	1.528 (3)
C2—C10	1.529 (3)	C11—C12	1.518 (4)
C2—C14	1.550 (3)	C12—C13	1.511 (4)
C3—C4	1.532 (3)	C13—C14	1.536 (3)
C4—C4a	1.493 (3)	C15—C16	1.532 (3)
C4—C9	1.528 (3)		
C15—N1—C8a	120.1 (2)	C7—C6—C5	121.6 (2)
C15—N1—C2	121.5 (2)	C7—C6—Cl1	119.7 (2)
C8a—N1—C2	118.3 (2)	C5—C6—Cl1	118.8 (2)
N1—C2—C3	107.3 (2)	C6—C7—C8	119.0 (2)
N1—C2—C10	110.3 (2)	C7—C8—C8a	120.4 (2)
C3—C2—C10	110.3 (2)	C8—C8a—C4a	120.4 (2)
N1—C2—C14	108.5 (2)	C8—C8a—N1	121.3 (2)
C3—C2—C14	110.9 (2)	C4a—C8a—N1	118.2 (2)
C10—C2—C14	109.5 (2)	C11—C10—C2	113.1 (2)
C2—C3—C4	113.4 (2)	C12—C11—C10	112.2 (2)
C4a—C4—C9	113.7 (2)	C13—C12—C11	112.0 (2)
C4a—C4—C3	105.0 (2)	C12—C13—C14	111.0 (2)
C9—C4—C3	111.3 (2)	C13—C14—C2	110.7 (2)
C5—C4a—C8a	118.9 (2)	O1—C15—N1	124.0 (2)
C5—C4a—C4	124.6 (2)	O1—C15—C16	119.9 (2)
C8a—C4a—C4	116.1 (2)	N1—C15—C16	116.0 (2)
C4a—C5—C6	119.5 (2)	C15—C16—Cl2	111.1 (2)

Data collection: *P*4 software. Cell refinement: *XSCANS* (Siemens, 1991). Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93.

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Low-temperature phase of bis(2-methoxycarbonyl-2-methylpropyl) 2,5-diisopropylidene-3,4-bis(2-methoxycarbonyl-2-methylpropoxycarbonyl)hex-3-enedioate, a crystal structure with six independent pseudo-related molecules

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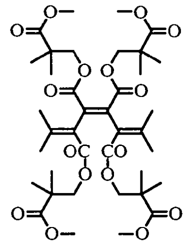
Abstract

The crystal structure of the title compound, $C_{38}H_{56}O_{16}$, is disordered above 298 K. A tripling of the unit cell is observed on cooling. The structure at 136 K contains six ordered molecules related by pseudo-translation vectors of $(\frac{1}{3},0,-\frac{1}{3})$, pseudo-inversion centers and pseudo-twofold screw axes.

Comment

The title compound, (I), shows a reversible phase transition at about 298 K. A data set collected at about 305 K revealed a monoclinic unit cell with $a = 12.254(2)$, $b = 26.241(4)$, $c = 13.461(3)$ Å, $\beta = 93.52(3)°$ and $V = 4320(1)$ Å^3 with $Z = 4$. The systematic absences showed the space group to be $P2_1/n$. The resulting structure, however, was seriously disordered, especially in the side chains. Below the phase-transition temperature a new unit cell is found with a volume three times as large as the high-temperature cell. The cell constants transform according to $a_{\rm low} = 2a_{\rm high} + c_{\rm high}$, $b_{\rm low} = b_{\rm high}$ and $c_{\rm low} = -a_{\rm high} + c_{\rm high}$. To collect data of the low-temperature phase a crystal mounted on a glass fiber was slowly cooled to 136 K. The $h0l$ reflections were absent for l odd. The $0k0$ reflections with k odd were weak but not absent. Thus, the space group is either Pc or $P2/c$. The structure was determined in the Pc space group.



(I)

The resulting structure has six independent molecules in the asymmetric unit. All six molecules are ordered at low temperature. The crystal structure contains no twofold axes parallel to the b axis. Thus the resulting structure can not be transformed to the centrosymmetric space group $P2/c$. The tripling of the unit cell below the phase-transition point results in pseudo-translation vectors of approximately $(\frac{1}{3},0,\frac{2}{3})$ and $(\frac{2}{3},0,\frac{1}{3})$ which relate molecule A with molecules C and F, and molecule B with molecules D and E.

The conformations of the six molecules are very similar, except for the relative orientations of the side chains. The conformations of molecules B and C are identical. Molecule B can be transformed to molecule C by a pseudo-inversion center at 0.438,0.251,0.303. This pseudo-inversion center also relates the major part of molecule A to molecule D and the major part of molecule E to molecule F. Some side chains of those molecules, however, are not fitted by this pseudo-center. The conformations of molecules D and F are also almost identical, but differ considerably from the conformations of molecules B and C. In effect, molecule D can be transformed to molecule F by a pseudo-inversion center at 0.281,0.250,0.471. This pseudo-center also relates the major part of molecule A to molecule B and a large part of molecule C to molecule E. Again a number of side chains of those molecules are not fitted by this pseudo-center.

The conformations of molecules A and E are unique. The side chains attached to C7, C10 and C17 of molecule A are very similar to those of molecules B and C. The corresponding side chains of molecule E on the other hand are very similar to those of molecules D