1-Acetyl-2a,8b-dichloro-1-methoxy-1,2,2a,8b-tetrahydro-3H-cyclobuta[c]chromen-3-one

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In the title compound, $C_{14}H_{12}Cl_2O_4$, the cyclobutane ring is folded. There are intermolecular Cl···O and C—H···O interactions in the crystal structure.

Comment

We have investigated the photo-induced reaction of 3,4-dichlorocoumarin and 2,3-dimethoxy-1,3-butadiene and obtained the title compound, (I), as one of the products. As part of this study, we have undertaken the X-ray crystallographic analysis of (I) in order to elucidate the structure of this cycloadduct.

(I)
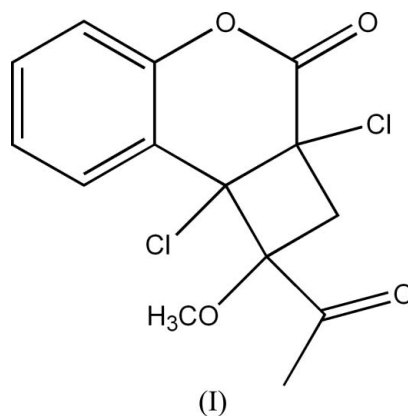
The bond lengths and angles in (I) are in good agreement with expected values, except for the C3—C14 [1.581 (4) Å] bond length. Owing to the presence of the Cl atom and methoxy group, this bond is longer than the mean Csp^3—Csp^3 distance [1.55 (2) Å] reported for cyclobutanes (Allen *et al.*, 1987). The cyclobutane ring is folded. The dihedral angle between the C3/C5/C14 and C5/C6/C14 planes is 31.4 (4)°. Atoms C7–C14, O4 are essentially coplanar; C6 deviates from this plane by 0.405 (5) Å. The two Cl atoms lie on the same side of the coumarin ring system.

In the crystal structure of (I), molecules are linked by intermolecular Cl1···O4($\frac{3}{2} - x$, $y - \frac{1}{2}$, $\frac{3}{2} - z$) [3.080 (3) Å] interactions. Similar interactions are observed in the related compound 4a,4c,9 b,9c-tetrahydro-4 b,4c,9 b,9c-tetrachloro-cyclobuta[1,2-*a*:3,4-*a'*]diindene-5,10-dione (Zhang *et al.*, 2003). These short contacts, together with intermolecular C—H···O interactions (Table 2) and van der Waals forces, stabilize the crystal structure.

Experimental

Compound (I) was prepared by the photo-induced reaction of a benzene solution (60 ml) of 3,4-dichlorocoumarin (3 mmol) with an

excess amount of 2,3-dimethoxy-1,3-butadiene (30 mmol), irradiated by light of wavelength longer than 300 nm for 7 h. It was isolated by column chromatography of the reaction mixture after evaporation of the solvent on silica gel. Single crystals of (I) were obtained by slow evaporation of a petroleum ether–ethyl acetate (1:3) solution (yield 23%).

Crystal data

$C_{14}H_{12}Cl_2O_4$
$M_r = 315.14$
Monoclinic, $P2_1/n$
$a = 12.678$ (3) Å
$b = 8.7360$ (17) Å
$c = 13.185$ (3) Å
$\beta = 107.09$ (3)°
$V = 1395.8$ (6) Å^3
$Z = 4$

$D_x = 1.500$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.0$–26.0°
$\mu = 0.47$ mm^{-1}
$T = 293$ (2) K
Block, colorless
$0.43 \times 0.33 \times 0.28$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*XCAD4*; Harms & Wocadlo, 1995)
$T_{min} = 0.813$, $T_{max} = 0.876$
2851 measured reflections
2727 independent reflections

1870 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 26.0°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = -15 \rightarrow 15$
3 standard reflections
  every 200 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.140$
$S = 1.00$
2727 reflections
181 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C6	1.772 (3)	C3—C14	1.581 (4)
Cl2—C14	1.787 (3)	C5—C6	1.524 (4)
O3—C7	1.203 (4)		
C3—O2—C4	114.5 (3)	C1—C2—C3	117.5 (3)
C7—O4—C8	123.0 (2)	O2—C3—C2	111.3 (2)
Cl1—C6—C7—O4	−103.1 (3)	Cl1—C6—C14—Cl2	−37.0 (3)

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
C4—H4$A\cdots$O3^{i}	0.96	2.55	3.468 (5)	159

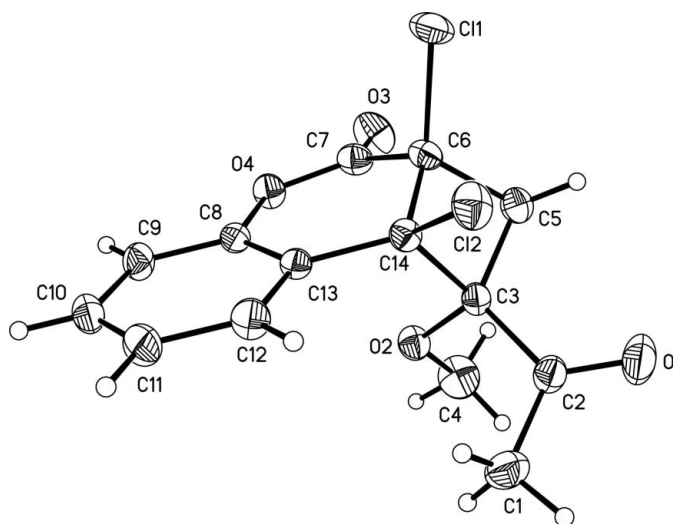Symmetry code: (i) $-x + 2, -y + 1, -z + 1$.

Figure 1
The structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

The H atoms were included in the riding-model approximation, with C—H distances of 0.93, 0.96 and 0.97 Å for aromatic, methyl and methylene H atoms, respectively, and with $U_{iso}(H) = 1.2U_{eq}$(aromatic and methylene C) or $1.5U_{eq}$(methyl C).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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