Table 2. *Selected geometric parameters (Å, °)*

N—C3	1.326 (2)	O1—C2	1.440 (2)
N—C1	1.441 (2)	O2—C3	1.219 (2)
O1—C3	1.347 (2)	C1—C2	1.516 (2)
C3—N—C1	112.6 (1)	O2—C3—N	128.9 (1)
C3—O1—C2	109.0 (1)	O2—C3—O1	120.8 (1)
N—C1—C2	100.9 (1)	N—C3—O1	110.3 (1)
O1—C2—C1	105.3 (1)		
C3—N—C1—C2	11.9 (2)	C1—N—C3—O1	−5.3 (2)
C3—O1—C2—C1	11.7 (1)	C2—O1—C3—O2	175.6 (1)
N—C1—C2—O1	−13.6 (1)	C2—O1—C3—N	−4.4 (1)
C1—N—C3—O2	174.6 (1)		

Non-H atoms were refined with anisotropic temperature factors. Positions and isotropic temperature factors were refined for H atoms. *PLATON*94 (Spek, 1990) was used for the geometry analysis of the structure. All computations were performed on IBM RS/6000 machines of the Namur Scientific Computing Facilities (SCF) centre.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *PLATON*94.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1055). Services for accessing these data are described at the back of the journal.

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1-(4-Chlorobenzoyloxy)-2-methoxy-4-(2-propenyl)benzene

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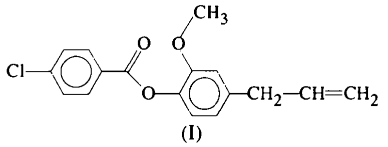
Abstract

In the title compound, 2-methoxy-4-(2-propenyl)phenyl 4-chlorobenzoate, $C_{17}H_{15}ClO_3$, the allyl group is observed to be in a disordered state. The two C atoms of the allyl group occupy two sets of sites in unequal proportions (68:32). The dihedral angle between the two aromatic rings is 71.64 (10)°.

Comment

The structure of the title compound, (I), was determined as part of our studies on the synthesis and characterization of this type of compound. An *ORTEP*II (Johnson, 1976) drawing of the molecular structure of (I) with the atomic labellling is shown in Fig. 1.



(I)

The phenyl rings and central carbonyl moiety in the molecule are similar to those described in the literature (Blake, Fallis, Parsons, Schröder & Bruce, 1996). The dihedral angle between the planes of the chlorophenyl and methoxyphenyl rings is 71.64 (10)°, and these two planes make angles of 10.3 (2) and 81.90 (9)°, respectively, with the plane of the central carbonyl moiety. The methoxy C14 atom deviates by 0.101 (6) Å

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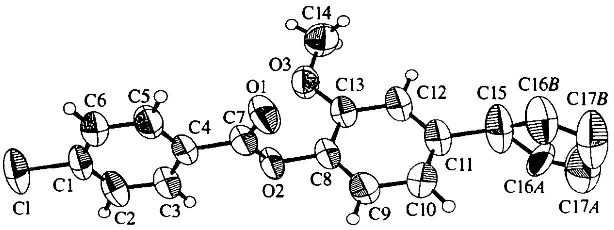

Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms of the allyl group have been omitted for clarity.

from the plane of the phenyl ring. The methoxy O atom, however, is in the plane of the phenyl ring. These three planes are planar within experimental error. The chlorophenyl moiety in the molecule is comparable to literature examples (Özbey, Kendi, Hocaoğlu, Uyar & Mak, 1993). The Cl—C1 bond length is 1.754 (3) Å. The other relevant bond lengths, angles and selected torsion angles are listed in Table 1.

The displacement parameters of atoms C15, C16 and C17 of the allyl group are quite high, resulting in unusual bond lengths involving these atoms. It is worthwhile considering the possibility of disorder in the chains near their ends (Işîk *et al.*, 1997). In the allyl group, the C15—C16*A* and C15—C16*B* single-bond distances [1.359 (7) and 1.302 (13) Å, respectively] are shorter than expected since this moiety has disorder with C16*A*/C17*A* and C16*B*/C17*B* in 68:32 proportions. The C15—C16*A*—C17*A* and C15—C16*B*—C17*B* angles are 137.5 (10) and 148 (2)°, respectively.

Experimental

The title compound was prepared by mixing a 1:1 molar ratio of 2-methoxy-4-(2-propenyl)phenol and 4-chlorobenzoyl chloride in NaOH solution. Colourless crystals appeared and single crystals suitable for X-ray diffraction analysis, grown from ethyl alcohol at room temperature, were obtained after 8 h.

Crystal data

$C_{17}H_{15}ClO_3$
$M_r = 302.74$
Triclinic
$P\bar{1}$
$a = 8.101\ (2)$ Å
$b = 10.321\ (2)$ Å
$c = 11.145\ (2)$ Å
$\alpha = 65.96\ (3)°$
$\beta = 72.40\ (3)°$
$\gamma = 65.93\ (3)°$
$V = 766.6\ (3)$ Å^3
$Z = 2$
$D_x = 1.312$ Mg m^{-3}
$D_m = 1.310$ Mg m^{-3}
D_m measured by pycnometry
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.91–18.12°$
$\mu = 0.256$ mm^{-1}
$T = 293\ (2)$ K
Prismatic
0.35 × 0.30 × 0.28 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2179 measured reflections
2179 independent reflections
1842 reflections with $I > 2\sigma(I)$
$\theta_{max} = 23.31°$
$h = 0 \rightarrow 8$
$k = -9 \rightarrow 11$
$l = -11 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: <2%

Refinement

Refinement on F^2
$R(F) = 0.0658$
$wR(F^2) = 0.1883$
$S = 1.084$
2179 reflections
258 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1247P)^2 + 0.1799P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.332$ e Å^{-3}
$\Delta\rho_{min} = -0.410$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.084 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cl—C1	1.754 (3)	C4—C7	1.497 (4)
O1—C7	1.184 (3)	C11—C15	1.542 (4)
O2—C7	1.348 (3)	C15—C16*B*	1.302 (13)
O2—C8	1.421 (3)	C15—C16*A*	1.359 (7)
O3—C13	1.357 (3)	C16*A*—C17*A*	1.244 (14)
O3—C14	1.413 (4)	C16*B*—C17*B*	1.10 (3)
C7—O2—C8	116.5 (2)	C16*B*—C15—C11	121.6 (6)
C13—O3—C14	117.5 (3)	C16*A*—C15—C11	117.2 (4)
O1—C7—O2	123.1 (2)	C17*A*—C16*A*—C15	137.5 (10)
O1—C7—C4	125.3 (3)	C17*B*—C16*B*—C15	148 (2)
O2—C7—C4	111.6 (2)		
C8—O2—C7—O1	5.3 (4)		
C8—O2—C7—C4	−174.2 (2)		
C3—C4—C7—O1	169.9 (3)		
C7—O2—C8—C9	−103.1 (3)		
C14—O3—C13—C8	−176.0 (3)		
C11—C15—C16*A*—C17*A*	−124.5 (12)		
C11—C15—C16*B*—C17*B*	107 (3)		

Corrections were made for the Lorentz and polarization factors, but not for absorption. The structure was solved by direct methods. The H atoms of C16 and C17 were added in calculated positions and refined using a riding model. The positions of other H atoms were obtained from the difference Fourier map. Anisotropic displacement parameters were used for all non-H atoms, while H atoms were given isotropic displacement parameters. All atoms of the allyl group were refined with anisotropic displacement parameters with the following restraint within the allyl group: the difference in the mean-square displacements along the bond direction of a bonded pair of atoms should not exceed 0.01 Å with an e.s.d. of 0.01 Å.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1013). Services for accessing these data are described at the back of the journal.

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Configuration of the Diels–Alder Adduct of Hexachlorocyclopentadiene with L-Menthyl Acrylate

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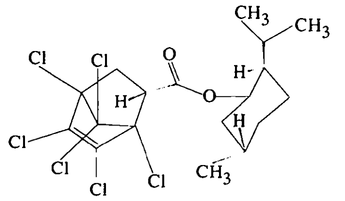
Abstract

The structure of the title compound, *endo*-(2*R*)-(–)-L-menthyl 1,4,5,6,7,7-hexachloro-4-norbornene-2-carboxylate, consists of discrete $C_{18}H_{22}Cl_6O_2$ molecules related by a twofold screw axis. The relative configuration was determined and the chirality at the unknown centres was assigned on the basis of the known chiral centres of L-menthene. Both the average Csp^2—Cl, 1.689 (5), and Csp^3—Cl, 1.753 (3) Å, distances are a little shorter than the literature values. The six-membered ring of the L-menthyl group has a chair conformation. C—O bond lengths in the carboxylate group are 1.194 (7) and 1.323 (7) Å.

Comment

Enantiomers of the cycloadducts of hexachlorocyclopentadiene (HCC) and the derivatives of acrylic acids show considerable differences in biological activity (Miyazaki, Hotta, Marumo & Sakai, 1978; Miyazaki, Sakai & Marumo, 1979, 1980). The derivatives of the Diels–Alder adduct of HCC can be used as building blocks for the synthesis of antibiotics, phytotoxins and functionalized carbocyclic nucleoside analogues (Berger, Rabiller, Königsberger, Faber & Griengl, 1990; Duke & Wells, 1987). It was also reported that the asymmetric thermal Diels–Alder reactions with chiral dienophiles L-menthyl acrylate and L-menthyl allyl ether gave cycloadducts of HCC up to 15% optical yield of predominant enantiomer (Akhmedov, Peynircioğlu, Mamedov, Tanyeli & Demir, 1994). Milder reaction conditions achieved by the use of Lewis-acid catalysts (BF_3.OEt, BBr_3, $SnCl_4$, $AlCl_3$) increased the optical yields up to 2.8-fold. The adducts with opposite configurations were obtained by using L-menthyl acrylate in catalyzed or uncatalyzed reactions.



The reaction of HCC with L-menthyl acrylate in the presence of $TiCl_4$ in *o*-xylene gave the Diels–Alder products in 60% yield. The product was characterized using IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The X-ray structure determination was performed to determine the configuration of the title compound (1). As can be seen from Fig. 1, the conformation is *endo*-(2*R*)-(–)-L-menthyl 1,4,5,6,7,7-hexachloro-4-norbornene-2-carboxylate. That the (–)-isomer of the product has an (*R*) configuration is shown for the first time as a result of this study. Previously, the (*R*) product was obtained only by thermal Diels–Alder reactions (Akhmedov *et al.*, 1994). The $TiCl_4$ catalyzed reaction seems to be proceeding through completely different transition states compared with the other Lewis-acid-catalyzed reactions.

The unit cell consists of two discrete $C_{18}H_{22}Cl_6O_2$ molecules related by a twofold screw axis. The closest intermolecular contact is 2.44 Å between H121 and H172(x, y, z + 1). In hexachloronorbornene the C—C bond distances are as expected. Both the average Csp^2—Cl, 1.689 (5), and Csp^3—Cl, 1.753 (3) Å, distances are a little shorter than the literature values, 1.734 (19) and 1.849 (11) Å (average), respectively, given by Allen *et al.* (1987). The distances of the cross-linking atoms C1, C4 and C7 to the best plane through C2, C3, C5, C6 are 0.818 (5), 0.826 (5) and 1.886 (5) Å, respectively. The