

of the CAD-4 diffractometer (purchased under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey).

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References

- Blake, A. J., Fallis, I. A., Parsons, S., Schröder, M. & Bruce, D. W. (1996). *Acta Cryst.* **C52**, 194–197.
- Enraf–Nonius (1993). *CAD-4 EXPRESS*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MOLÉN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- İşık, Ş., Aygün, M., Şaşmaz, S., Kendi, E., Büyükgüngör, O. & Erdönmez, O. (1996). *Acta Cryst.* **C53**, 593–594.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Özbey, S., Kendi, E., Hocaoglu, N., Uyar, T. & Mak, T. C. W. (1993). *Acta Cryst.* **C49**, 2165–2167.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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

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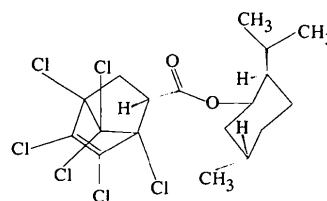
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Abstract

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 C₁₈H₂₂Cl₆O₂ 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 Csp²–Cl, 1.689 (5), and Csp³–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, phytochemicals 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 (BF₃·OEt, BBr₃, SnCl₄, AlCl₃) 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 TiCl₄ in *o*-xylene gave the Diels–Alder products in 60% yield. The product was characterized using IR, ¹H NMR and ¹³C 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 TiCl₄ 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 C₁₈H₂₂Cl₆O₂ 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 Csp²–Cl, 1.689 (5), and Csp³–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

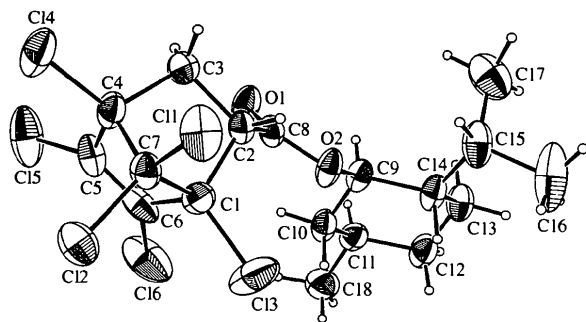


Fig. 1. ORTEP (Johnson, 1965) drawing of C₁₈H₂₂Cl₆O₂ with the atomic labelling scheme. Thermal ellipsoids are drawn at the 40% probability level. H atoms are shown as small circles with arbitrary radii.

dihedral angle between the C2, C3, C5, C6 and the C1, C4, C7 planes is 90.9 (3)°.

The ring (C9–C14) of the L-menthyl group has a chair conformation. The total puckering amplitude of the ring is 0.561 (5) Å. The L-menthyl moiety consisting of C14, C16, C17, C15 atoms is a flat trigonal pyramid with C15 occupying the apical position at a distance of 0.437 (6) Å from the basal plane. The C—O bond distances in the central bridge of the molecule, C8—O1 = 1.194 (7), C8—O2 = 1.323 (7) and O2—C9 = 1.473 (6) Å, agree well with those found in other compounds containing menthyl esters, such as that described by Saba, Adovasio & Nardelli (1992), which are 1.194 (3), 1.332 (4) and 1.476 (3) Å (average), respectively, for the same distances. Also, the total puckering amplitude of the menthyl ring given by Saba *et al.* (1992), 0.567 (3) Å (average), agrees with that found in the present compound.

Experimental

A mixture of L-menthyl acrylate (10.5 g, 50 mmol) and hexachlorocyclopentadiene (13.6 g, 50 mmol) in the presence of TiCl₄ in *o*-xylene in a sealed tube was heated for 8 h at 433 K. After removal of unreacted starting materials by distillation, crystals were grown from methanol solution.

Crystal data

C₁₈H₂₂Cl₆O₂
M_r = 483.09
 Monoclinic
*P*2₁
a = 8.8496 (13) Å
b = 14.8198 (19) Å
c = 8.3661 (14) Å
 β = 92.221 (5)°
V = 1096.4 (7) Å³
Z = 2
D_x = 1.463 Mg m⁻³
D_m not measured

Mo K α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 10.09–18.35°
 μ = 0.798 mm⁻¹
T = 295 K
 Prism
 0.40 × 0.35 × 0.30 mm
 Brown

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical via ψ scans (MolEN; Fair, 1990)
T_{min} = 0.727, *T_{max}* = 0.785
 2321 measured reflections
 2171 independent reflections

2104 reflections with $I > \sigma(I)$
 R_{int} = 0.009
 θ_{max} = 26.32°
 h = -11 → 7
 k = 0 → 18
 l = -10 → 10
 3 standard reflections
 frequency: 120 min
 intensity decay: -0.58%

Refinement

Refinement on *F*
 R = 0.049
 wR = 0.056
 S = 1.18
 2104 reflections
 240 parameters
 H atoms riding, see text
 $w = 1/[\sigma(F^2) + (0.02F)^2 + 1.5]$, except $w = 0$ if $F^2 < \sigma(F^2)$

$(\Delta/\sigma)_{\text{max}}$ = <0.001
 $\Delta\rho_{\text{max}}$ = 0.557 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.149 e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

C11—C7	1.777 (6)	O1—C8	1.194 (7)
C12—C7	1.753 (5)	O2—C8	1.323 (7)
C13—C1	1.742 (6)	O2—C9	1.473 (6)
C14—C4	1.744 (6)	C1—C6	1.531 (9)
C15—C5	1.689 (7)	C2—C8	1.523 (7)
C16—C6	1.691 (6)	C5—C6	1.31 (1)
C1—C2—C3	102.7 (4)	C14—C15—C16	111.5 (7)
C4—C5—C6	108.6 (5)	C14—C15—C17	114.3 (6)
C11—C7—C12	107.0 (3)	C16—C15—C17	110.7 (7)
C1—C7—C4	93.1 (4)		

All non-H atoms were refined with anisotropic thermal parameters. H atoms were placed geometrically 0.95 Å from the parent C atoms. The H atoms of the L-menthyl group were refined for a few cycles and then a riding model was used for all H atoms with $U(\text{H}) = 1.3U_{\text{eq}}(\text{C})$.

Data collection and cell parameters: *CAD-4-Express* (Enraf–Nonius, 1990). Data reduction, program used to solve structure, program used to refine structure, molecular graphics and software used to prepare material for publication: *MolEN* (Fair, 1990). Other programs used include *PLATON* (Spek, 1990) and *PARST96* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1283). Services for accessing these data are described at the back of the journal.

References

- Akhmedov, I. M., Peynircioğlu, B., Mamedov, E. G., Tanyeli, C. & Demir, A. S. (1994). *Tetrahedron*, **50**, 2099–2106.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Berger, B., Rabiller, C. G., Königsberger, K., Faber, K. & Griengl, H. (1990). *Tetrahedron Asymm.* **1**, 541–546.

Duke, C. C. & Wells, R. J. (1987). *Aust. J. Chem.* **40**, 1641–1654.

Enraf–Nonius (1993). *CAD-4-Express Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Miyazaki, A., Hotta, T., Marumo, S. & Sakai, M. (1978). *J. Agric. Food Chem.* **26**, 975–977.

Miyazaki, A., Sakai, M. & Marumo, S. (1979). *J. Agric. Food Chem.* **27**, 1403–1405.

Miyazaki, A., Sakai, M. & Marumo, S. (1980). *J. Agric. Food Chem.* **28**, 1310–1311.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Saba, A., Adovasio, V. & Nardelli, M. (1992). *Tetrahedron Asymm.* **3**, 1573–1582.

Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.

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Hydrogen-Bonding Pattern of an α,β -Unsaturated δ -Keto Acid: 1',3'-Dihydro-2-methyl-6-oxospiro[2-cyclohexene-1,2'-2'H-indene]-3-carboxylic Acid

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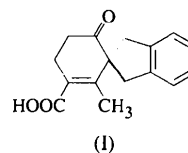
Abstract

The title compound, $C_{16}H_{16}O_3$, adopts a chiral conformation incorporating a flattened cyclohexene ring, with pairs of molecules forming centrosymmetric carboxyl dimers. The acid group is rotated $18(1)^\circ$ from coplanarity with the alkene and displays typical carboxyl disorder; the methyl group is rotationally disordered.

Comment

Our continuing study of the X-ray structures of simple keto carboxylic acids concerns their hydrogen-bonding motifs, of which four are known. The commonest has acid dimers in which the ketone is not involved (Coté, Thompson & Lalancette, 1996). Less frequently, intermolecular carboxyl-to-ketone hydrogen bonds repeat, often along a screw axis, to yield a catemer (Coté, Thompson & Lalancette, 1997). A third rare arrangement has an internal hydrogen bond (Coté, Lalancette

& Thompson, 1996) and one instance is known of acid-to-ketone dimerization (Abell, Trent & Morris, 1991). The title compound, (I), is a δ -keto acid, a class found to contain examples of both dimeric and catemeric, as well as internal, hydrogen bonding.



The atom-numbering scheme for (I) and the chiral conformation it adopts are shown in Fig. 1. Around the planar alkene, whose $C1-C2=C3-C4$ torsion angle is $-0.9(4)^\circ$, the six-membered ring assumes a conformation which is more flattened than a standard cyclohexene half-chair because of the sp^2 hybridization at the C6 atom. The ketonic C6 atom lies only $0.282(2)$ Å out of the average plane of this ring [the $C3=C2-C1-C6$ torsion angle is $9.4(3)^\circ$], while C5 lies $0.332(1)$ Å from this plane, on the opposite face [torsion angle $C2=C3-C4-C5$ is $21.5(3)^\circ$]. The indane system is planar, with a mean deviation from planarity of 0.016 Å, and nearly orthogonal to the plane defined by the C6, C1 and C2 atoms [dihedral angle $89.0(1)^\circ$]. The methyl group H atoms are rotationally disordered, with contributions from two principal rotamers in a ratio of $76(3):24(3)$; the predominant rotamer is shown in Fig. 1.

The carboxyl group is rotated slightly out of the plane defined by the alkene and its two neighboring ring C atoms ($C1-C2=C3-C4$), forming a dihedral angle of $18(1)^\circ$. Its C—O bond lengths and C—C—O angles are partially averaged by disordering, as is frequently found in dimeric carboxylic acids (Leiserowitz, 1976). The observed lengths here are $C7-O2$ $1.229(3)$ and $C7-O3$ $1.263(3)$ Å, and the angles are $116.6(2)$ for $C3-C7-O3$ and $123.6(3)^\circ$ for $C3-C7-O2$. Typical values for highly ordered cases are 1.21 and 1.31 Å, and 112 and 123° , respectively (Borthwick, 1980).

It is possible that the disordering exhibited by both the methyl and carboxyl groups is coupled, since these two groups are physically quite close. Modeling with a fully ordered carboxyl (Borthwick, 1980) in the two orientations (differing by 180°) contributing to the carboxyl disorder shows that the modeled C—O oxygen approaches significantly closer to the methyl H atoms than does the modeled C=O oxygen. For the worst-case 'head-on' steric interaction involving the modeled C—O oxygen and the minor (24%) methyl conformer (not shown in Fig. 1), our model indicates an $O\cdots H$ distance on the order of 1.8 Å. The serious repulsion involved would force the staggering of the H atoms to either side of the C—O oxygen, as seen in the major methyl conformer (76%), where their modeled $O\cdots H$ distances become roughly 2.15 and 2.50 Å to H8B and H8C, respectively. For the modeled C=O oxy-