

(1SR,2SR,3SR,10SR,12RS,13RS,14RS,17SR)-13-Hydroxy-11-oxapentacyclo[8.7.0.0^{2,14}.0^{4,9}.0^{12,17}]-heptadeca-4,6,8-trien-3-yl 4-chlorobenzoate**Reşat Ustabaş,^a Ufuk Çoruh,^b Abdullah Menzek,^c Aliye Altundaş,^c Metin Yavuz^d and Tuncer Hökelek^{e*}**^aDepartment of Physics, Graduate School of Natural and Applied Sciences, Ondokuz Mayıs University, Kurupelit 55139, Samsun, Turkey, ^bDepartment of Computer Education and Instructional Technology, Educational Faculty, Ondokuz Mayıs University, 55200 Atakum-Samsun, Turkey, ^cDepartment of Chemistry, Faculty of Arts and Sciences, Atatürk University, 25240 Erzurum, Turkey, ^dDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, Kurupelit 55139, Samsun, Turkey, and ^eDepartment of Physics, Hacettepe University, Beytepe 06800, Ankara, Turkey

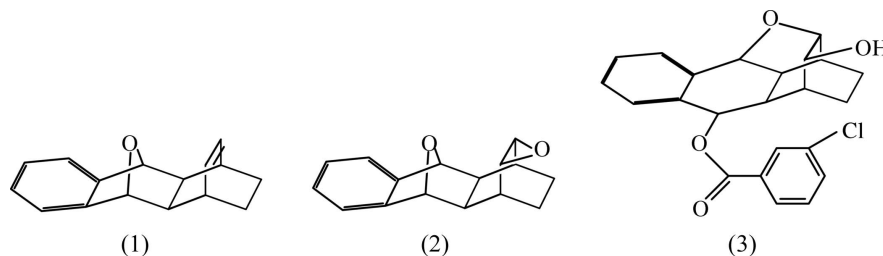
Correspondence e-mail: ucoruh@omu.edu.tr

Key indicatorsSingle-crystal X-ray study
 $T = 100\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.044
 wR factor = 0.157
Data-to-parameter ratio = 13.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $\text{C}_{23}\text{H}_{21}\text{ClO}_4$, the bicyclic system has approximate D_3 symmetry and the four non-planar six-membered rings adopt boat conformations. Intra- and intermolecular hydrogen bonds are effective in stabilizing the crystal structure.

Comment

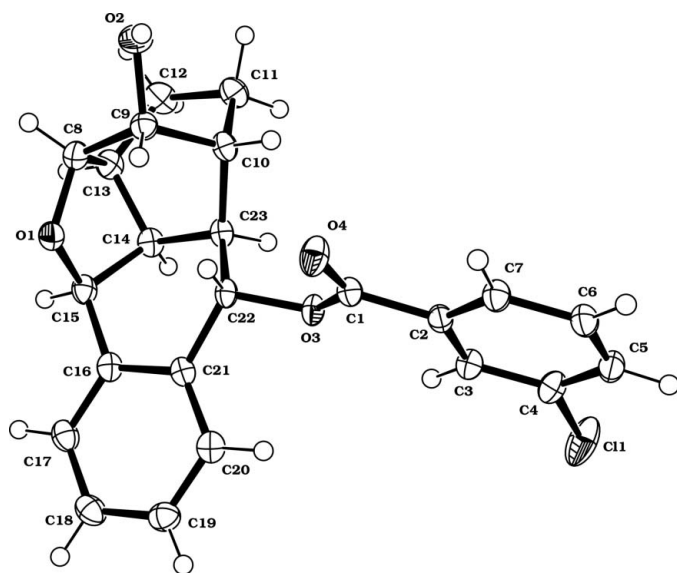
Compound (1) was obtained from the cycloaddition reaction of oxobenzonorbornadiene with cyclohexadiene; it has one double bond and 1,4-epoxide as a functional group (Menzek *et al.*, 2004). Such systems are important and undergo reactions such as rearrangement (Menzek *et al.*, 1997; Altundaş *et al.*, 2000; Menzek, 2000; Daştan, 2001; Menzek & Gökmen, 2002; Menzek & Karakaya, 2004). Compound (1) was reacted with *m*-chloroperbenzoic acid (*m*-CPBA) in chloroform at room temperature; compound (2) and the hydroxyester (3), which is a rearranged product, were isolated from the reaction mixture. Acid- and base-catalysed reactions of 1,2-epoxides are useful procedures for preparing compounds with vicinal functional groups such as diols (Solomon, 1988). To explain the mechanisms of the rearrangement reactions, the structures of products such as (3) should be established.



The title compound, (3), contains a central non-planar six-membered carbon ring with a chlorobenzoic acid substituent bonded to atom C22 (Fig. 1). A benzene ring is fused on one side and a bicyclic system is fused on the other side. The bicyclic system is bridged, through atom O1, to the central ring, forming a five-membered (O1/C8/C13–C15) ring (ring A). This bridging causes significant distortions in the tetrahedral angles: C8–C13–C12 = 112.66 (11)°, C8–C13–C14 = 97.53 (10)° and C12–C13–C14 = 115.79 (12)°. Overall, the bond lengths and angles are normal.

In the bicyclic system, the six-membered rings *B* (C8–C13), *C* (C8–C10/C23/C13/ C14) and *D* (C13/C14/C23/C10–C12) adopt boat conformations with puckering parameters (Cremer & Pople, 1975) $\varphi_2 = 105.03(1)^\circ$, $\theta_2 = 86.6(1)^\circ$ and $Q_T = 0.820(1)\text{ \AA}$ (for ring *B*), $\varphi_2 = 39.98(8)^\circ$, $\theta_2 = 139.82(8)^\circ$ and $Q_T = 1.114(1)\text{ \AA}$ (for ring *C*) and $\varphi_2 = -175.55(1)^\circ$, $\theta_2 =$

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Figure 1

An ORTEP-3 (Farrugia, 1997) drawing of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 70% probability level.

84.4 (1)° and $Q_T = 0.786$ (1) Å (for ring *D*). Furthermore, the central ring *E* (C21–C23/C14/C16) also adopts a boat conformation, with φ_2 43.1 (1)°, $\theta_2 = 96.5$ (1)° and $Q_T = 0.554$ (1) Å.

As can be seen from the torsion angles (Table 1) and the puckering parameters, the bicyclic system has approximate D_3 symmetry; the deviation from ideal D_3 symmetry is evidenced by the dihedral angles between the planes *F* (C13/C14/C23/C10), *G* (C10/C11/C12/C13) and *H* (C8/C9/C10/C13) [$F/G = 56.28$ (7)°, $F/H = 60.26$ (6)° and $G/H = 57.62$ (6)°].

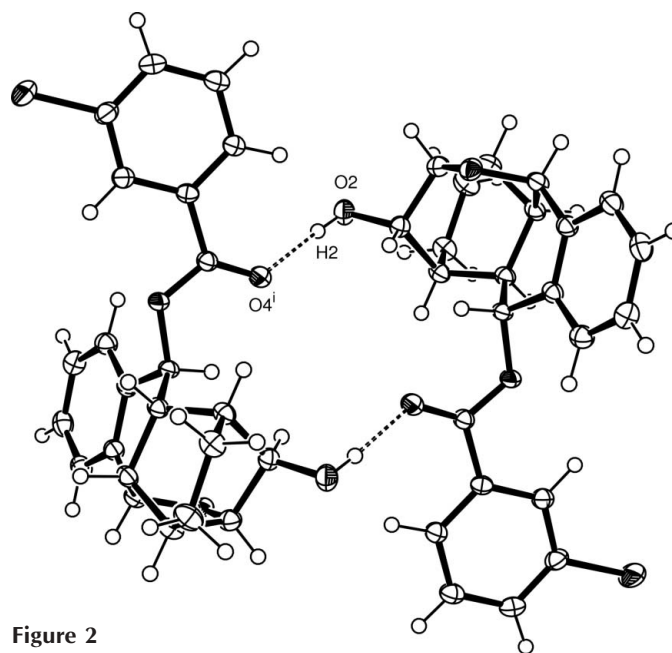
The intermolecular hydrogen bond between the hydroxyl H atom of the bicyclic system and the carboxyl O atom, as well as an intramolecular C–H...O hydrogen bond (Table 2 and Fig. 2), are effective in stabilizing the crystal structure.

Experimental

Compound (1) (1.164 g, 5.2 mmol) was added to a solution of *m*-chloroperbenzoic acid (2.392 g, 10.4 mmol). After stirring at room temperature for 1 d, the reaction mixture was washed with a solution of NaOH (0.5%, 500 ml) and water (500 ml), and dried over Na_2SO_4 ; the solvent was then evaporated. The reaction mixture was crystallized from CHCl_3 /diethyl ether and epoxide (2) (0.735 g, 59%) was obtained as colorless crystals. The residue was submitted to preparative thick-layer chromatography (PLC) with ethyl acetate/hexane (1:1). The epoxide (2) (yield 0.150 mg, 12%) and compound (3) (yield 0.468 g, 9%, mp. 405–407 K) were obtained.

Crystal data

$\text{C}_{23}\text{H}_{21}\text{ClO}_4$	$D_x = 1.429 \text{ Mg m}^{-3}$
$M_r = 396.85$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 28900 reflections
$a = 13.6103$ (5) Å	$\theta = 1.9$ – 28.0°
$b = 12.5787$ (6) Å	$\mu = 0.24 \text{ mm}^{-1}$
$c = 21.6102$ (8) Å	$T = 100 \text{ K}$
$\beta = 94.479$ (3)°	Prism, colorless
$V = 3688.4$ (3) Å ³	$0.30 \times 0.20 \times 0.15 \text{ mm}$
$Z = 8$	


Figure 2

The hydrogen bonding (dashed lines) in (II).

Data collection

Stoe IPDS-II diffractometer
 φ scans
 Absorption correction: integration
 (*X-RED*; Stoe & Cie, 2002)
 $T_{\min} = 0.912$, $T_{\max} = 0.954$
 30714 measured reflections
 4371 independent reflections

3806 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$
 $\theta_{\text{max}} = 27.8^\circ$
 $h = -17 \rightarrow 17$
 $k = -16 \rightarrow 16$
 $l = -28 \rightarrow 28$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.157$
 $S = 0.71$
 4371 reflections
 337 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.68 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.56 \text{ e } \text{Å}^{-3}$

Table 1

Selected torsion angles (°).

C11–C10–C9–C8	71.42 (13)	C12–C13–C8–C9	–43.52 (15)
C23–C10–C9–C8	–47.27 (13)	C14–C13–C8–C9	78.53 (12)
C11–C10–C23–C14	–61.62 (13)	C12–C13–C14–C23	52.58 (15)
C23–C10–C11–C12	66.69 (14)	C14–C13–C12–C11	–48.17 (16)

Table 2

Hydrogen-bond geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O2–H2...O4 ⁱ	0.83 (3)	2.02 (3)	2.8478 (15)	171 (3)
C22–H22...O4	0.94 (2)	2.25 (2)	2.7382 (16)	111 (1)

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

All H atoms were located in a difference synthesis and refined isotropically [$C\text{—}H = 0.87$ (2)– 1.03 (2) Å].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s)

used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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