Instrumental Achievements

Crystal Structure of 5,6,7,10-Tetrahydro-3-methoxy-2,9-dimethyl-benzocyclooctene-5-carboxylic Acid

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The benzocyclooctene carboxylic acid **1** is a key intermediate in our recent total synthesis of the sesquiterpene parvifolin **2**.¹ Because of its importance within the synthetic scheme, an unambiguous proof of its structure became necessary and we have undertaken the X-ray crystal analysis of this compound. The six-membered ring to which the methoxy and methyl groups are attached shows normal geometry: 1.386(4) Å and 120.0(3)° for the mean C–C distance and internal angle, respectively. The eight-membered ring adopts a distorted boat conformation. The molecules are hydrogen-bonded between carboxyl groups forming centrosymmetric dimers. The O(3)···O(2) and H(3)···

O(2) distances are 2.651(3) and 1.78(4) Å and the O(3)—H···O(2) angle is 172(4)°. The H atoms of the CH, CH₂ and CH₃ groups were assigned coordinates based on the

1, Z = CO₂H, R = CH₃

2, Z = CH₃, R = H

Fig. 1 Chemical structure.

Table 1 Crystal and experimental data

Formula: C ₁₆ H ₂₀ O ₃
Formula weight=260.33
Crystal system: monoclinic
Space group: P2 ₁ /n Z=4
a=11.975(7) Å
b=7.938(3) Å
c=15.903(8) Å
β=105.66(4)°
V=1456(1) Å ³
D _x =1.19 g/cm ³
μ(Cu Kα)=6.15 cm ⁻¹
T=293 K
colorless
F(000)=560
0.22×0.18×0.28 mm
Radiation=Cu Kα
R=0.053
R _w =0.073
No. of reflections used=1477
No. of parameters=176
Goodness-of-fit=1.79
Measurement: Nicolet P3/F
Program system: TEXSAN
Structure determination: direct methods
Refinement: full matrix

Table 2 Final coordinates (×10⁴) and equivalent isotropic temperature factors (Å²)

Atom	x	y	z	B _{eq}
O1	7308(2)	932(3)	8098(1)	6.9(1)
O2	4728(2)	2999(2)	4928(1)	5.9(1)
O3	4146(2)	4790(2)	5789(1)	5.7(1)
C1	4365(2)	558(3)	8218(2)	4.5(1)
C2	5560(2)	497(4)	8447(2)	4.9(1)
C3	6116(2)	971(4)	7828(2)	4.7(1)
C4	5484(2)	1463(3)	7000(2)	4.3(1)
C5	3602(2)	1953(3)	5854(2)	4.1(1)
C6	3372(2)	369(4)	5289(2)	5.1(1)
C7	2899(3)	-1075(3)	5720(2)	5.1(1)
C8	1766(2)	-703(4)	5912(2)	5.0(1)
C9	1544(2)	234(3)	6539(2)	4.5(1)
C10	2399(2)	1217(3)	7244(2)	4.5(1)
C11	3697(2)	1084(3)	7397(1)	3.9(1)
C12	4283(2)	1526(3)	6786(2)	3.8(1)
C13	6240(3)	-42(5)	9347(2)	7.8(2)
C14	7937(3)	1441(6)	7517(3)	9.2(2)
C15	4213(2)	3285(3)	5474(2)	4.3(1)
C16	0331(2)	410(4)	6613(2)	6.3(1)

$$B_{eq} = (8\pi^2/3) [U_{22} + U_{11} + U_{33} + 2U_{13}\cos\beta]$$

Fig. 2 Molecular conformation and atom numbering scheme of 5,6,7,10-tetrahydro-3-methoxy-2,9-dimethyl benzocyclooctene-5-carboxylic acid.

Table 3 Bond distances (Å) and angles (°)

O1	C3	1.376(3)	C5	C6	1.527(4)
O1	C14	1.400(4)	C5	C12	1.524(4)
O2	C15	1.214(3)	C5	C15	1.503(4)
O3	C15	1.306(3)	C6	C7	1.520(4)
C1	C2	1.379(4)	C7	C8	1.499(4)
C1	C11	1.398(4)	C8	C9	1.327(4)
C2	C3	1.382(4)	C9	C10	1.515(4)
C2	C13	1.505(4)	C9	C16	1.495(4)
C3	C4	1.386(4)	C10	C11	1.511(4)
C4	C12	1.387(4)	C11	C12	1.388(3)

C3	O1	C14	119.0(2)	C7	C8	C9	129.8(2)
C2	C1	C11	123.3(2)	C8	C9	C10	127.8(2)
C1	C2	C3	117.9(2)	C8	C9	C16	120.5(3)
C1	C2	C13	121.2(3)	C10	C9	C16	111.7(2)
C3	C2	C13	120.9(3)	C9	C10	C11	122.9(2)
O1	C3	C2	115.5(2)	C1	C11	C10	118.4(2)
O1	C3	C4	123.9(2)	C1	C11	C12	117.4(2)
C2	C3	C4	120.6(2)	C10	C11	C12	124.2(2)
C3	C4	C12	120.5(2)	C4	C12	C5	119.6(2)
C6	C5	C12	110.7(2)	C4	C12	C11	120.4(2)
C6	C5	C15	111.8(2)	C5	C12	C11	119.9(2)
C12	C5	C15	110.9(2)	O2	C15	O3	122.7(2)
C5	C6	C7	112.7(2)	O2	C15	C5	123.6(2)
C6	C7	C8	114.3(2)	O3	C15	C5	113.7(2)

expected bonding geometry. The H atom attached to the O(3) atom was found in a difference Fourier map and was included in the final cycles of refinement. All H atoms had a fixed isotropic temperature factor, $U=0.06 \text{ Å}^2$.

Contribution No. 1178 of the Instituto de Química, UNAM.

This research was supported by a Grant-in-Aid for Scientific Research No. 1304-E9205 from CONACYT, México.

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(Received December 17, 1992)

(Accepted April 15, 1993)