Crystal structure of dimethyl (1α,2β,3α,4β,7β,8α,9β,10α)-13-isopropylidene-pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-diene-2,9-dicarboxylate, $C_{21}H_{24}O_4$

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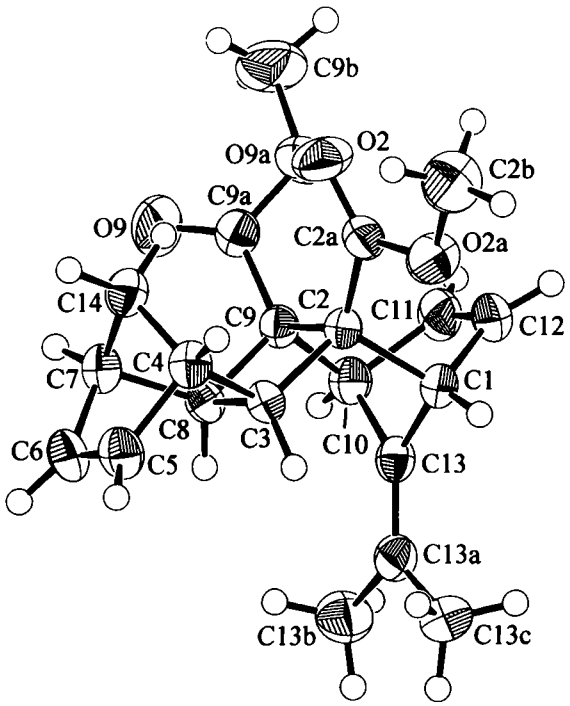

Abstract

$C_{21}H_{24}O_4$, monoclinic, $P12_1/n1$ (No. 14), a = 9.547(2) Å, b = 19.014(3) Å, c = 9.877(2) Å, β = 91.42(2)°, V = 1792.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.062, $wR_{ref}(F^2)$ = 0.194, T = 293 K.

Source of material

$LiClO_4$ (11 mg, 5 mol%) was added to a solution of Smith's diene [(1α,2β,5β,6α)dimethyl tricyclo[4.2.1.0^{2,5}]nona-3,7-diene-3,4-dicarboxylate] (500 mg, 2.14 mmol) and 6,6-dimethylfulvene (1.1 g, 10.4 mmol) in dichloromethane (3 ml). The solution was stirred at room temperature for two days under nitrogen. Further dichloromethane was added (10 ml) and the solution washed with water. The organic fraction was dried (Na_2SO_4) and the solvent removed under reduced pressure. The resultant residue was separated by column chromatography; elution with petroleum spirit removed excess dimethylfulvene before the crude product was eluted with 1:1 EtOAc/petroleum spirit. Combined fractions were taken to dryness to give an oil which was triturated with MeOH to precipitate polymeric impurities. The MeOH solution was taken to dryness to give adduct which was recrystallised from petroleum spirit; yield: 456 mg (64.5%); mp 378 K – 379 K. ^{1}H and ^{13}C NMR as well as EIMS results are included in the deposited CIF-file.

Experimental details

The C-bound H atoms were placed in their geometrically calculated positions and included in the final refinement in the riding model approximation.

Discussion

The molecule adopts a staircase motif with successive risers being defined by C11–C12, C1–C13–C10, C2–C9, C3–C8, C4–C14–C7 and C5–C6 connectivities. The ester groups lie to the opposite side of the molecule to the C=CMe$_2$ group.

Table 1. Data collection and handling.

Crystal:	colourless, multifacted, size 0.29 × 0.32 × 0.40 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	0.86 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC6R, $\omega/2\theta$
$2\theta_{max}$:	50.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3370, 3175
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2196
$N(param)_{refined}$:	227
Programs:	SHELXS-86 [1], SHELXL-97 [2], teXsan [3], DIBABS [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	–0.1983	0.2420	–0.2055	0.091(3)
H(2a)	4e	0.0739	0.4138	–0.2227	0.109(4)
H(2b)	4e	0.1930	0.3721	–0.2939	0.109
H(2c)	4e	0.1829	0.3704	–0.1358	0.109
H(3)	4e	–0.1232	0.1875	–0.4430	0.091
H(4)	4e	0.1057	0.2488	–0.5248	0.091
H(5)	4e	–0.0126	0.1840	–0.7191	0.073(2)
H(6)	4e	0.0263	0.0583	–0.6903	0.073
H(7)	4e	0.1728	0.0380	–0.4775	0.091
H(8)	4e	–0.0815	0.0679	–0.4092	0.091
H(9a)	4e	0.3542	0.1214	0.0786	0.109
H(9b)	4e	0.4121	0.0997	–0.0626	0.109

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(9c)	4e	0.3310	0.0447	0.0240	0.109
H(10)	4e	-0.1131	0.0345	-0.1467	0.091
H(11)	4e	-0.0578	0.1006	0.0683	0.073
H(12)	4e	-0.1087	0.2238	0.0336	0.073
H(13a)	4e	-0.4670	0.0390	-0.3486	0.109
H(13b)	4e	-0.3870	0.0155	-0.2156	0.109

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(13c)	4e	-0.3103	0.0148	-0.3542	0.109
H(13d)	4e	-0.5089	0.1469	-0.3746	0.109
H(13e)	4e	-0.3812	0.1968	-0.3983	0.109
H(13f)	4e	-0.4582	0.1987	-0.2600	0.109
H(14a)	4e	0.2820	0.1516	-0.5456	0.091
H(14b)	4e	0.2459	0.1580	-0.3897	0.091

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(2)	4e	0.2278(2)	0.2427(1)	-0.2101(3)	0.036(1)	0.050(1)	0.100(2)	-0.005(1)	-0.011(1)	-0.013(1)
O(2a)	4e	0.0401(2)	0.3109(1)	-0.2297(3)	0.047(1)	0.030(1)	0.080(2)	-0.002(1)	-0.000(1)	-0.005(1)
O(9)	4e	0.2287(3)	0.0320(2)	-0.2207(3)	0.072(2)	0.075(2)	0.069(2)	0.041(2)	-0.014(1)	-0.012(1)
O(9a)	4e	0.2076(3)	0.1149(1)	-0.0653(2)	0.061(2)	0.075(2)	0.052(2)	0.016(1)	-0.024(1)	-0.011(1)
C(1)	4e	-0.1432(3)	0.2001(2)	-0.1820(3)	0.034(2)	0.036(2)	0.036(2)	0.004(1)	0.005(1)	-0.004(1)
C(2)	4e	-0.0005(3)	0.1911(1)	-0.2570(3)	0.031(1)	0.031(2)	0.034(2)	0.003(1)	0.001(1)	-0.004(1)
C(2a)	4e	0.1039(3)	0.2485(2)	-0.2270(3)	0.040(2)	0.035(2)	0.035(2)	-0.001(1)	0.001(1)	-0.005(1)
C(2b)	4e	0.1300(4)	0.3719(2)	-0.2197(5)	0.069(2)	0.035(2)	0.100(3)	-0.012(2)	0.007(2)	-0.008(2)
C(3)	4e	-0.0270(3)	0.1772(1)	-0.4124(3)	0.036(2)	0.029(1)	0.029(1)	-0.000(1)	0.002(1)	-0.001(1)
C(4)	4e	0.0846(3)	0.1985(2)	-0.5172(3)	0.040(2)	0.034(2)	0.037(2)	-0.003(1)	0.006(1)	0.004(1)
C(5)	4e	0.0290(3)	0.1623(2)	-0.6439(3)	0.052(2)	0.048(2)	0.028(2)	0.001(2)	0.006(1)	0.004(1)
C(6)	4e	0.0505(3)	0.0932(2)	-0.6282(3)	0.055(2)	0.045(2)	0.030(2)	0.002(2)	0.006(1)	-0.005(1)
C(7)	4e	0.1216(3)	0.0822(2)	-0.4906(3)	0.043(2)	0.033(2)	0.036(2)	0.004(1)	0.006(1)	-0.001(1)
C(8)	4e	0.0015(3)	0.0971(1)	-0.3916(3)	0.037(2)	0.028(1)	0.030(1)	-0.001(1)	0.001(1)	-0.000(1)
C(9)	4e	0.0320(3)	0.1100(2)	-0.2372(3)	0.034(1)	0.032(2)	0.030(2)	0.004(1)	0.001(1)	-0.000(1)
C(9a)	4e	0.1674(3)	0.0819(2)	-0.1781(3)	0.041(2)	0.042(2)	0.035(2)	0.004(1)	0.002(1)	0.004(1)
C(9b)	4e	0.3369(5)	0.0934(3)	-0.0010(4)	0.064(3)	0.122(4)	0.061(3)	0.012(3)	-0.027(2)	0.007(3)
C(10)	4e	-0.0958(3)	0.0852(2)	-0.1494(3)	0.041(2)	0.037(2)	0.033(2)	0.001(1)	0.005(1)	0.003(1)
C(11)	4e	-0.0818(3)	0.1218(2)	-0.0139(3)	0.050(2)	0.058(2)	0.030(2)	0.004(2)	0.007(1)	0.001(1)
C(12)	4e	-0.1096(3)	0.1892(2)	-0.0329(3)	0.044(2)	0.054(2)	0.034(2)	0.000(2)	0.006(1)	-0.009(1)
C(13)	4e	-0.2116(3)	0.1298(2)	-0.2133(3)	0.036(2)	0.036(2)	0.032(1)	-0.000(1)	0.008(1)	0.000(1)
C(13a)	4e	-0.3308(3)	0.1137(2)	-0.2773(3)	0.037(2)	0.046(2)	0.040(2)	-0.004(1)	0.008(1)	-0.004(1)
C(13b)	4e	-0.3781(4)	0.0390(2)	-0.3011(4)	0.053(2)	0.057(2)	0.067(2)	-0.016(2)	0.004(2)	-0.006(2)
C(13c)	4e	-0.4286(3)	0.1690(2)	-0.3325(4)	0.039(2)	0.064(2)	0.058(2)	0.005(2)	-0.006(2)	-0.005(2)
C(14)	4e	0.2079(3)	0.1497(2)	-0.4803(3)	0.039(2)	0.045(2)	0.040(2)	0.001(1)	0.008(1)	-0.001(1)

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