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Crystal structure of (4*aS*,5*S*,6*aS*,6*a*¹*S*, 10*aS*)-4*a*,5,6*a*,6*a*¹,9,10-hexahydro-7*H*-4,5-methanocyclobuta[4,5]naphtho[8*a*,1-*b*]pyran-6(2*H*)-one, C₁₅H₁₆O₂

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Abstract

C₁₅H₁₆O₂, triclinic, *P* $\bar{1}$ (no. 2), *a* = 5.6034(7) Å, *b* = 8.7105(11) Å, *c* = 12.5661(16) Å, α = 92.790(7)°, β = 100.516(7)°, γ = 106.105(6)°, *V* = 576.15(13) Å³, *Z* = 2, *R*_{gt}(*F*) = 0.0476, *wR*_{ref}(*F*²) = 0.1348, *T* = 296.15 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All reactions were carried out under argon atmosphere with dry solvents, unless otherwise noted. All the commercially chemicals were purchased and used without any

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.18 × 0.16 × 0.14 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.09 mm ^{−1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.5°, 99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	5634, 2869, 0.013
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 2588
<i>N</i> (<i>param</i>) _{refined} :	154
Programs:	Bruker [1], Olex2 [2]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C1	0.5765(2)	0.28624(13)	0.82412(9)	0.0285(2)
C2	0.5558(3)	0.26267(16)	0.94308(9)	0.0391(3)
H2A	0.5755	0.3660	0.9817	0.047*
H2B	0.6937	0.2231	0.9772	0.047*
C3	0.3021(3)	0.14482(18)	0.95458(11)	0.0467(3)
H3A	0.3258	0.1014	1.0241	0.056*
H3B	0.1780	0.2034	0.9547	0.056*
C4	0.1998(3)	0.00867(16)	0.86580(12)	0.0446(3)
H4	0.0476	−0.0689	0.8658	0.053*
C5	0.3241(2)	−0.00193(14)	0.78757(11)	0.0384(3)
C6	0.2710(3)	−0.08108(16)	0.67263(12)	0.0494(3)
H6A	0.0979	−0.0989	0.6335	0.059*
H6B	0.3238	−0.1777	0.6668	0.059*
C7	0.4652(2)	0.07387(15)	0.64600(10)	0.0388(3)
H7	0.5952	0.0493	0.6112	0.047*
C8	0.5586(2)	0.12234(13)	0.77144(9)	0.0320(2)
H8	0.7116	0.0909	0.7989	0.038*
C9	0.3424(3)	0.18610(16)	0.58708(10)	0.0424(3)
C10	0.2093(2)	0.27689(16)	0.64884(10)	0.0372(3)
H10	0.0339	0.2155	0.6488	0.045*
C11	0.3650(2)	0.35065(13)	0.76518(9)	0.0300(2)
H11	0.2509	0.3617	0.8137	0.036*
C12	0.2343(3)	0.45022(18)	0.61695(12)	0.0487(3)
H12A	0.2835	0.4689	0.5475	0.058*
H12B	0.0897	0.4882	0.6230	0.058*
C13	0.4513(3)	0.50382(15)	0.71406(11)	0.0406(3)
C14	0.6835(3)	0.60222(16)	0.73953(13)	0.0502(3)
H14	0.7365	0.6923	0.7034	0.060*
C15	0.8560(3)	0.55846(15)	0.83100(12)	0.0469(3)
H15A	1.0308	0.6164	0.8307	0.056*
H15B	0.8185	0.5895	0.8998	0.056*
O1	0.3476(3)	0.20177(19)	0.49237(9)	0.0831(5)
O2	0.82422(15)	0.38882(10)	0.82021(7)	0.0375(2)

further purification. The 4-(but-3-yn-1-yl)phenol was prepared according to the literature. The 4-(but-3-yn-1-yl)-4-(prop-2-yn-1-yloxy)cyclohexa-2,5-dien-1-one was synthesized: To a well-stirred mixture of 4-(but-3-yn-1-yl)phenol (1.0 equiv, 10 mmol) and propargyl alcohol (15 mL) was added phenyliodine(III) diacetate (1.5 equiv, 15 mmol) at 0 °C in several portions. The mixture was warmed to room temperature and stirred overnight followed by quenching with the saturated aqueous NaHCO₃ (40 mL) and the saturated aqueous Na₂SO₃ (20 mL) and extracted with ethyl acetate (30 mL) for three times. The combined organic mixture was washed with brine (30 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate eluent to afford 4-(but-3-yn-1-yl)-4-(prop-2-yn-1-yloxy)cyclohexa-2,5-dien-1-one.

The 4-(buta-2,3-dien-1-yloxy)-4-(penta-3,4-dien-1-yl)cyclohexa-2,5-dien-1-one was synthesized: To a well-stirred solution of 4-(but-3-yn-1-yl)-4-(prop-2-yn-1-yloxy)cyclohexa-2,5-dien-1-one (2.0 mmol, 1.0 equiv) in dioxane (10 mL) was sequentially added paraformaldehyde (300 mg, 10 equiv), CuBr (114.8 mg, 0.4 equiv) and diisopropylamine (0.56 mL, 4.0 equiv). The resulting mixture was stirred at 110 °C for about 3 h. After cooled to room temperature, the reaction mixture was filtered through celite and followed by washing with DCM (10 mL) for three times. The organic phase was concentrated under reduced pressure and the residue was purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to afford the 4-(buta-2,3-dien-1-yloxy)-4-(penta-3,4-dien-1-yl)cyclohexa-2,5-dien-1-on.

The title compound: To a 25 mL Schlenk tube equipped with magnetic stirring bar were added the 4-(buta-2,3-dien-1-yloxy)-4-(penta-3,4-dien-1-yl)cyclohexa-2,5-dien-1-on (100.2 mg) and TFE (2.0 mL). The tube was sealed and the resulting mixture was stirred for 50 h at 200 °C, before being cooled to r.t., and the mixture was transferred to a flask and concentrated under reduced pressure. The resulting sticky oil was purified by column chromatography on silica gel using the petroleum ether/ethyl acetate as the eluent to afford the title compound (86.4 mg, 86% yield) as a colourless foamy solid.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Comment

The cyclobutanes and the cyclobutenes derivatives containing polycyclic compounds are very communly in natural

products and bioactive compounds, [3] and there are numerous methods for the construction of the cyclobutane and the cyclobutenes derivatives using methods of photochemistry [4], transition metal catalysis [5] and the Lewis acids [6] and the thermally promoted cycloaddition reaction [7]. Recently, we disclosed a powerful, distinct, and atom-economical method for the synthesis of clobutane-fused oxygen contained tricyclic framework via a thermally promoted intramolecular [2 + 2] cycloaddition of cyclohexadienone-tethered allenes [8]. However, the method for the dicyclobutanes containing ring system remains rather rare reported to date. As our continuing efforts on the development of efficient synthetic methods for cyclic compounds synthesis associated with allenes [9], herein, we report the thermally promoted double [2+2] cycloaddition for the synthesis of dicyclobutanes containing poly-ring system, furthermore, the crystal structure of the polycycle compound was also reported.

There is one molecule in the asymmetric unit of the title structure (see the figure). The single crystal structure verifies that all bond lengths are in normal ranges. Furthermore, the crystal packing doesn't exhibit intramolecular or intermolecular hydrogen bonding and the classical interactions.

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