Crystal Structure of Ethyl-1-phenyl-2-trimethylsilanyl-3-oxo-3H-Benzo[b]cyclobuta[d]pyran-2a(8bH)-carboxylate

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The title compound, C₂₃H₂₄O₄Si, was synthesized by photo-induced reactions and characterized by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic space group *Pbca*, with *a*=9.7299(2), *b*=19.6064(4), *c*=21.6264(5) Å, *V*=4125.63(15) Å³, *Z*=8 and *D_x* 1.264 g cm⁻³. The dihedral angle between the cyclobutene and the attached benzene ring is 38.04(13)°. The molecules are linked into an infinite chain along the *a*-axis. The crystal structure is stabilized by weak C-H...O and C-H...π interactions.

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The photo [2 + 2] cycloaddition of olefins with 3-substituted coumarins has been receiving recent interest.¹ In our ongoing research work on photoinduced electron transfer (PET) reactions between trimethylsilylphenylacetylene and different electron acceptors, we prepared the title compound, (I), by photoinduced reactions of trimethylsilylphenylacetylene with 3-ethoxycarbonylcoumarin in an acetonitrile solution. As a part of this study, we undertook an X-ray crystallographic analysis of (I) in order to elucidate its structure and steric configuration.

The title compound, (I), was obtained by the photoinduction of 3-ethoxycarbonylcoumarin with 2 equivalence of trimethylsilylphenylacetylene in an acetonitrile solution. It was isolated by silica-gel column chromatography of the reaction mixture after evaporation of the solvent. Single crystals of (I) suitable for x-ray data collection were obtained by slow evaporation of an acetone-petroleum ether (2:1 v/v) solution (40.0% yield).

The crystallographic and experimental parameters used for data collection and determination of the structure are given in Table 1. All non-hydrogen atoms were refined anisotropically. All H atoms were placed at calculated positions with the C-H distances in the range 0.93–0.96 Å. The *U*_{iso} values were constrained to be 1.5*U*_{eq} of the carrier atoms for hydroxyl and methyl H atoms, and 1.2*U*_{eq}(C) for the remaining H atoms. The

highest residual electron density peak ($\Delta\rho_{\max}$) is located at 0.38 Å from H11A, and the deepest hole ($\Delta\rho_{\min}$) is located at 0.73 Å from C18. The final refinement converged well. Selected bond lengths, bond angles and torsions angles are given in Table 2 and show normal values.² An ORTEP plot of the molecule at 50% probability is shown in Fig. 2. In the structure of (I), the

Table 1 Crystal and experimental data

Chemical formula: C ₂₃ H ₂₄ O ₄ Si
Formula weight: 392.51
Crystal system: orthorhombic
Space group: <i>Pbca</i> , <i>Z</i> = 8
<i>a</i> = 9.7299(2) Å
<i>b</i> = 19.6064(4) Å
<i>c</i> = 21.6264(5) Å
<i>V</i> = 4125.63(15) Å ³
<i>D_x</i> = 1.264 g cm ⁻³
μ (Mo <i>K</i> α) = 0.140 mm ⁻¹
<i>T</i> = 100.0(1) K
<i>F</i> (000) = 1664
Crystal size = 0.57 × 0.17 × 0.08 mm
θ range for data collection 1.88 to 26.99°
<i>R</i> = 0.0763
<i>R_w</i> = 0.1929
No. of unique data measured = 4497
No. of observed data with [<i>I</i> ≥ 2σ(<i>I</i>)] = 3868
No. of parameters = 257
Goodness-of-fit = 1.073
($\Delta\rho$) _{max} = 1.241 e.Å ⁻³
($\Delta\rho$) _{min} = -0.367 e.Å ⁻³
Measurements: Bruker APEX2 CCD diffractometer ³
Program system: Apex2 ³
Structure determination: direct method(SHELXTL) ⁴
Refinement: full-matrix least-squares

CCDC 654133 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Fig. 1 Chemical structure of (I).

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Table 2 Selected bond lengths (Å) bond angles (°) and torsion angles (°)

Si1-C22	1.852(3)	C6-C7	1.469(3)
Si1-C23	1.859(3)	C7-C17	1.358(3)
Si1-C21	1.865(3)	C7-C8	1.531(3)
Si1-C17	1.890(2)	C8-C9	1.481(3)
O1-C15	1.354(3)	C8-C16	1.569(3)
O1-C14	1.393(3)	C15-C16	1.511(3)
O2-C15	1.207(3)	C16-C18	1.517(3)
O3-C18	1.205(3)	C16-C17	1.549(3)
O4-C18	1.335(3)	C19-C20	1.502(4)
O4-C19	1.461(3)		
C22-Si1-C23	110.26(13)	C18-O4-C19	116.34(19)
C22-Si1-C21	109.11(12)	C17-C7-C8	96.25(19)
C22-Si1-C17	108.10(11)	C7-C8-C16	84.73(17)
C21-Si1-C17	110.23(11)	C17-C16-C8	87.36(17)
C15-O1-C14	122.93(19)	C7-C17-C16	91.65(19)
C1-C6-C7-C8	141.9(2)	C9-C8-C16-C18	124.4(2)
C17-C7-C8-C9	115.3(2)	C15-C16-C17-Si1	59.5(3)
C6-C7-C8-C9	-65.3(3)	C18-C16-C17-Si1	-69.3(3)
C7-C8-C9-C14	-87.4(3)	C8-C16-C18-O3	89.8(3)
O1-C15-C16-C17	93.0(2)	C15-C16-C18-O4	47.0(3)

Fig. 2 Molecular structure of (I) with the atomic-numbering scheme. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level.

environment of Si1 is tetrahedral, the C8-C14/O1/C15-C16 ring is essentially planar with the maximum deviation of $-0.106(2)$ Å

Table 3 Hydrogen-bonding geometry (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
C8-H8A...O3 ⁱ	0.98	2.4686	3.546(3)	147
C23-H23A...Cg1 ⁱⁱ	0.96	3.2482	3.546(3)	100
C23-H23C...Cg1 ⁱⁱ	0.96	2.9542	3.546(3)	121

Cg1 is the centroid of C9-C14 benzene ring.

Symmetry codes: i = $1/2+x, y, 3/2-z$; ii = $2-x, -y, 1-z$

for atom C15. The C1-C6 benzene ring is twisted slightly away from the cyclobutene ring (C7/C8/C16/C17) with a dihedral angle of $38.05(15)^\circ$. The dihedral angle between the cyclobutene ring and the C9-C14 benzene ring is $68.42(14)^\circ$. The orientation of the ethylester group (C18/O3/O4/C19-C20) can be indicated by the torsion angle $C15-C16-C18-O4 = 47.0(3)^\circ$. In the crystal packing the molecules are stacked as chains down the *a*-axis. A weak C-H...O intermolecular interaction, C8-H8A...O3ⁱ (symmetry code: i = $1/2 + x, y, 3/2 - z$) (Table 3) is observed. C-H... π interactions involving C9-C14 benzene ring, namely C23-H23A...Cg1ⁱⁱ and C23-H23C...Cg1ⁱⁱ (symmetry code: ii = $2 - x, -y, 1 - z$), are observed; Cg1 is the centroid of C9-C14 benzene ring (Table 3). The crystal is stabilized by these weak C-H...O and C-H... π interactions.

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