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Crystal Structure of Cholesteryl Coumarin-3-Carbamate

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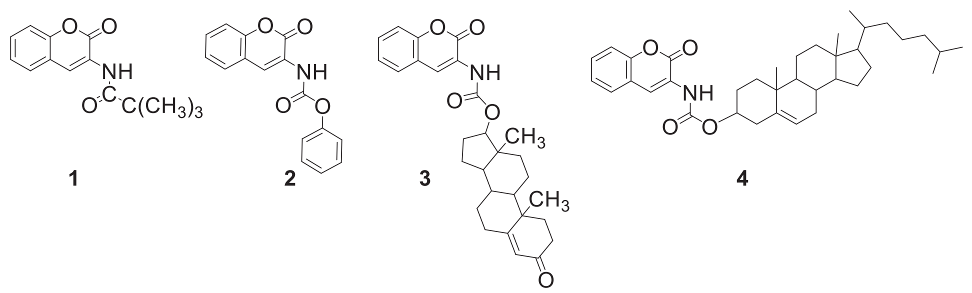
Abstract — Coumarin-3-carbamate derivatives were prepared by the reaction of the corresponding alcohols with coumarin-3-carbonyl azide. The testosterone and *t*-butyl derivatives have herbicidal activities, but the phenyl and cholesteryl derivatives have no herbicidal activities. The crystal structure of cholesteryl coumarin-3-carbamate was analyzed by X-ray crystallography. It crystallizes in the space group $P4_12_12$ (#92) with cell parameters a=10.110(2) Å, c=62.13(1) Å, Z=8, and V=6350(2) Å^3. The crystals of the testosterone derivative had intermolecular C—H · · · O and C—H · · · π interactions.

1. Introduction

The discovery and development of new herbicides is a long and difficult endeavor.[1–5] A large number of herbicides are currently available to assist in controlling weeds in a variety of crops. Herbicides can be classified into families based on their chemical structures and modes of action.[6] For examples, the carbamate herbicides inhibit protein biosynthesis and are effective in a gramineous weed. Coumarin is a chemical compound found in many plants, notably in high concentration in the Tonka bean woodruff and bison grass. The coumarin derivatives are an useful component for developing new materials such as fluorescence materials and laser dyes, nonlinear optical materials and reagents, photorefractive materials, photo resists, intermediates for drug synthesis, luminescence materials, and analytical reagents etc.[7–10]

Recently we have reported the synthesis and biological activities of coumarin-3-carbamate derivatives (**1**–**4**) as a new herbicide.[11] The *t*-butyl derivative (**1**) and testosterone derivative (**3**) found to be particularly effective herbicide against wild amaranth (*Amaranthus blitum L.*) and green foxtail (*Setaria viridis Beauv.*). Numerous studies have been dedicated to determining their structural investigation, in an effort to acertain the mechanism of action of herbicides.[12,13] Crystal structure analyses provide us with important information about intermolecular interaction.[14–17] We now report the structures of cholesteryl coumarin-3-carbamate (**4**) with the aim of



1 2 3 4

Fig. 1. Chemical structures of coumarin-3-carbamates (**1**–**4**).

contributing to a deeper understanding of the biological mechanism of action of the carbamate herbicides.

2. Experimental

2.1. Analysis

The melting points were obtained using a Yanagimoto micro-melting-point apparatus and are uncorrected. The NMR spectra were recorded using JEOL Lambda 400 and 600 spectrometers and solutions in CDCl$_3$ at room temperature; the chemical shifts are expressed in δ units. The stationary phase used in column chromatography was Wakogel C-300. The transition temperatures were measured by differential scanning calorimetry (Seiko DSC 200).

2.2. Material

Coumarin-3-carbamate derivatives (**1**–**4**) were prepared by the reaction of the corresponding alcohols such as t-butanol, phenol, testosterone, and cholesterol with coumarin-3-carbonyl azide as reported by the previous paper.11) The spectral data of **1**–**4** are given bellow.

1: colorless crystals, m.p. 96.5°C (measured by DSC). ^{1}H NMR (600 MHz, CDCl$_3$) δ =1.54 (9H, s), 7.28 (1H, dt, J=7.4, 1.02 Hz) 7.32 (1H, d, J=8.2 Hz), 7.39 (1H, ddd, J=8.2, 7.4, 1.4 Hz), 7.42 (1H, brs), and 7.47 (1H, dd, J=7.4, 1.4 Hz) 8.28 (1H, brs). ^{13}C NMR (150 MHz, CDCl$_3$) δ =28.19 (3C), 81.72, 116.26, 120.03, 120.38, 124.57, 125.06, 127.30, 128.98, 149.47, 152.46, and 158.62.

2: colorless crystals, m.p. 156.7°C (measured by DSC). ^{1}H NMR (600 MHz, CDCl$_3$) δ =7.21 (2H, d, J=.7.8 Hz), 7.28 (1H, t, J=7.8 Hz), 7.30 (1H, t, J=7.7 Hz), 7.35 (1H, d, J=7.7 Hz), 7.42 (2H, t, J=7.8 Hz), 7.45 (1H, t, J=7.7 Hz), 7.47 (1H, dd, J=7.7, 1.4 Hz), 7.88 (1H, brs), and 8.34 (1H, brs). ^{13}C NMR (150 MHz, CDCl$_3$) δ =116.37, 119.60, 121.43 (2C), 121.90, 125.19, 123.84, 126.08, 127.60, 129.50 (2C), 129.60, 149.76, 150.17, 151.50, and 158.38.

3: colorless crystals, m.p. 240.3°C (measured by DSC). ^{1}H NMR (600 MHz, $CDCl_3$) δ =0.881 (3H,s), 0.97 (1H, ddd, J=15.0, 10.8, 4.1 Hz), 1.06 (1H, m), 1.11 (1H, ddd, J=12.4, 11.1, 7.1 Hz), 1.205 (3H, s), 1.25 (1H, dt, J=13.0, 4.1 Hz), 1.36–1.47 (2H, m), 1.59–1.74 (5H, m), 2.04 (1H, ddd, J=13.5, 4.9, 3.2 Hz), 2.22–2.46 (7H, m), 4.65 (1H, t, J=8.8 Hz), 5.74 (1H, brs), 7.30 (1H, dt, J=7.6, 1.1 Hz), 8.31 (1H, brs), 7.33 (1H, d, J=8.3 Hz), 7.43 (1H, ddd, J=8.3, 7.6, 1.6 Hz), 7.48 (1H, dd, J=7.6, 1.6 Hz), and 7.55 (1H, brs). ^{13}C NMR (150 MHz, $CDCl_3$) δ =12.10, 17.38, 20.51, 23.40, 27.54, 31.43, 32.69, 33.91, 35.38, 35.69, 36.65, 38.59, 42.53, 50.11, 53.68, 84.11, 116.30, 119.86, 120.86, 123.96, 124.26, 125.14, 127.40, 129.23, 149.55, 153.30, 158.59, 170.83, and 199.44.

4: colorless prisms, m.p. 184.5°C (measured by DSC). ^{1}H NMR (600 MHz, $CDCl_3$) δ =0.69 (3H, s), 0.865 (3H, d, J=6.66 Hz), 0.87 (3H, d, J=6.66 Hz), 0.90–2.47 (35H, m), 4.62(1H, ddd, J=16.3, 11.2, 5.0 Hz), 5.42(1H, brs), 7.29 (1H, t, J=7.3 Hz), 7.32(1H, d, J=8.4 Hz), 7.42 (1H, ddd, J=8.4, 7.3, 1.2 Hz), 7.48 (1H, dd, J=7.3, 1.2 Hz), and 8.30 (1H, brs). ^{13}C NMR (150MHz, $CDCl_3$) δ =11.86, 18.70 19.31, 21.05, 22.56, 22.81, 23.83, 24.28, 27.94, 28.02, 28.23, 31.86, 31.92, 35.79, 36.18, 36.58, 36.92, 38.30, 39.58, 39.73, 42.32, 50.02, 56.15, 56.70, 75.84 116.30, 119.93, 120.73, 122.97, 124.38, 125.07, 127.40, 129.13, 139.41, 149.58, 152.83, and 158.53.

2.3. Data Collection

A colorless prism crystal of $C_{37}H_{51}NO_4$ having approximate dimensions of 0.200 x 0.200 x 0.100 mm was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Cu-Kα radiation. The crystal-to-detector distance was 127.40 mm. Cell constants and an orientation matrix for data collection corresponded to a primitive tetragonal cell (laue class: 4/mmm) with dimensions: a=10.110(2) Å, c=62.13(1) Å, V=6350 (2) Å^3. For Z=8 and $F. W.$=573.81, the calculated density is 1.200 g/cm^3. Based on the reflection conditions of: $h00$: h=2n, 00l: l=4n and the successful solution and refinement of the structure, the space group was determined to be: $P4_12_12$ (#92). The data were collected at a temperature of −160 ± 1°C to a maximum 2θ value of 136.5°. A total of 475 oscillation images were collected. A sweep of data was done using ω scans from 50.0 to 240.0° in 2.0° step, at χ =50.0° and ϕ =15.0°. The exposure rate was 40.2 [sec./°]. A second sweep was performed using ω scans from 50.0 to 240.0° in 2.0° step, at χ =50.0° and ϕ =90.0°. The exposure rate was 40.2 [sec./°]. Another sweep was performed using ω scans from 50.0 to 240.0° in 2.0° step, at χ =50.0° and ϕ =195.0°. The exposure rate was 40.2 [sec./°]. Another sweep was performed using ω scans from 50.0 to 240.0° in 2.0° step, at χ =50.0° and ϕ =285.0°. The exposure rate was 40.2 [sec./°]. Another sweep was performed using ω scans from 50.0 to 240.0° in 2.0° step, at χ =10.0° and ϕ =60.0°. The exposure rate was 40.2 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.200 mm pixel mode.

2.4. Data Reduction

Of the 20946 reflections that were collected, 3516 were unique (R_{int}=0.0400); equivalent reflections were merged. The linear absorption coefficient, μ, for Cu-Kα radiation is 5.992 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.781 to 0.942. The data were corrected for Lorentz and polarization effects.

2.5. Structure Solution and Refinement

The structure was solved by direct methods[18)] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement ($\Sigma\ w(F_o^2 - F_c^2)^2$ where w=Least Squares weights) on F^2 was based on 3516 observed reflections and 384 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of: $R_1 = \Sigma \|F_0| - |F_c\| / \Sigma |F_0| = 0.0586$, $wR_2 = [\Sigma (w(F_0^2 - F_c^2)^2) / \Sigma w(F_0^2)^2]^{1/2} =$ 0.1399. The standard deviation of an observation of unit weight (Standard deviation of an observation of unit weight: $[\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$ where: No=number of observations, Nv= number of variables) was 1.18. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.30 and −0.26 e^-/A^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[19)] Anomalous dispersion effects were included in F_{calc}[20)]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[21)] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[22)] All calculations were performed using the *CrystalStructure4.0*[23)] crystallographic software package except for refinement, which was performed using *SHELXL97*.[24)] Fractional atomic coordinates and equivalent isotropic displacement parameters were shown in Table 1. Anisotropic displacement parameters were shown in Table 2.

3. Result & Discussion

Coumarin-3-carbamate derivatives (**1**–**4**) were prepared by the reaction of the corresponding alcohol such as t-butanol, phenol, testosterone, and cholesterol with coumarin-3-carbonyl azide as reported by the previous paper.[11] As shown in Table 3, *t*-butyl derivative (**1**) and testosterone derivative (**3**) are particularly effective herbicide against wild amaranth (*Amaranthus blitum L.*) and green foxtail (*Setaria viridis Beauv.*), but the benzene derivative (**2**) and cholesteryl derivative (**4**) have no herbicidal activities for these weeds.

Table 1. Fractional atomic coordinates, equivalent isotropic displacement parameters (B_{iso}/B_{eq})

atom	x	y	z	B_{eq}
O1	−0.8219(4)	0.6557(4)	0.00017(5)	6.9(1)
O2	−0.7181(4)	0.4892(4)	0.01626(6)	8.5(2)
O3	−0.3558(3)	0.7964(4)	0.03205(5)	6.13(9)
O4	−0.3055(3)	0.5814(3)	0.03941(4)	4.74(7)
N1	−0.4960(4)	0.6243(5)	0.02385(5)	5.5(1)
C1	−0.7153(6)	0.6028(7)	0.01041(7)	6.6(2)
C2	−0.5997(5)	0.6912(7)	0.01355(6)	5.9(2)
C3	−0.6006(5)	0.8185(6)	0.00693(6)	6.6(2)
C4	−0.7169(5)	0.8688(7)	−0.00407(6)	6.8(2)
C5	−0.7254(5)	0.9990(7)	−0.01219(7)	8.9(2)
C6	−0.8374(6)	1.0358(8)	−0.02340(9)	10.0(3)
C7	−0.9416(6)	0.9530(8)	−0.02633(7)	8.3(2)
C8	−0.9367(5)	0.8238(7)	−0.01853(6)	7.2(2)
C9	−0.8249(6)	0.7847(7)	−0.00734(6)	6.4(2)
C10	−0.3829(5)	0.6792(7)	0.03172(6)	5.3(2)
C11	0.0598(4)	0.5450(4)	0.07520(5)	2.55(7)
C12	−0.0778(4)	0.5349(4)	0.08597(5)	3.24(8)
C13	−0.1896(4)	0.5090(4)	0.07025(5)	3.70(8)
C14	−0.1969(4)	0.6186(5)	0.05367(6)	3.73(8)
C15	−0.0661(4)	0.6282(4)	0.04138(5)	3.40(8)
C16	0.0501(4)	0.6443(4)	0.05667(5)	2.76(7)
C17	0.1411(4)	0.7374(4)	0.05336(5)	3.01(7)
C18	0.2613(4)	0.7580(4)	0.06684(5)	3.08(8)
C19	0.2903(4)	0.6418(4)	0.08192(5)	2.50(7)
C20	0.1600(3)	0.5953(4)	0.09214(5)	2.50(7)
C21	0.1814(4)	0.4966(4)	0.11083(5)	2.78(7)
C22	0.2850(4)	0.5425(4)	0.12726(5)	2.99(7)
C23	0.4175(4)	0.5724(4)	0.11637(5)	2.71(7)
C24	0.3890(4)	0.6803(3)	0.09930(5)	2.54(7)
C25	0.5264(4)	0.7284(4)	0.09267(5)	3.10(7)
C26	0.6065(4)	0.7241(4)	0.11360(5)	3.36(8)
C27	0.5223(4)	0.6449(4)	0.13042(5)	2.72(7)
C28	0.4772(4)	0.4470(4)	0.10623(5)	3.14(8)
C29	0.1007(4)	0.4084(3)	0.06600(5)	2.73(7)
C30	0.6097(4)	0.5629(4)	0.14575(5)	3.04(7)
C31	0.6972(4)	0.6555(4)	0.15931(6)	3.19(8)
C32	0.8162(4)	0.5919(4)	0.17029(5)	3.43(8)
C33	0.8861(4)	0.6899(4)	0.18481(6)	3.72(8)
C34	1.0139(5)	0.6442(5)	0.19539(7)	6.1(2)
C35	1.0644(6)	0.7538(7)	0.21042(6)	9.3(2)
C36	1.1201(5)	0.6103(5)	0.17932(9)	7.1(2)
C37	0.5322(4)	0.4732(4)	0.16089(6)	3.93(9)

$B_{eq}=8/3\pi^2(U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}(aa^*bb^*)\cos\gamma+2U_{13}(aa^*cc^*)\cos\beta+2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Anisotropic displacement parameters (Å^2)

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.086(3)	0.116(3)	0.059(2)	0.071(3)	−0.043(2)	−0.038(2)
O2	0.116(4)	0.100(3)	0.107(3)	0.074(3)	−0.075(3)	−0.058(3)
O3	0.057(3)	0.103(3)	0.073(2)	0.033(3)	0.011(2)	0.043(3)
O4	0.038(2)	0.086(3)	0.056(2)	0.024(2)	−0.004(2)	0.022(2)
N1	0.051(3)	0.117(4)	0.041(2)	0.045(3)	−0.005(2)	0.008(2)
C1	0.081(4)	0.117(5)	0.052(3)	0.072(4)	−0.040(3)	−0.039(4)
C2	0.059(4)	0.143(6)	0.023(2)	0.060(4)	0.000(2)	0.002(3)
C3	0.046(3)	0.161(6)	0.043(3)	0.046(4)	0.016(2)	0.048(3)
C4	0.047(4)	0.169(6)	0.043(3)	0.059(4)	0.021(3)	0.045(4)
C5	0.049(4)	0.202(7)	0.089(4)	0.052(4)	0.029(3)	0.103(5)
C6	0.054(4)	0.224(8)	0.103(5)	0.064(5)	0.040(4)	0.114(5)
C7	0.068(4)	0.202(8)	0.045(3)	0.083(5)	0.018(3)	0.045(4)
C8	0.070(4)	0.170(7)	0.036(3)	0.073(4)	−0.004(3)	−0.004(3)
C9	0.065(4)	0.149(6)	0.029(2)	0.071(4)	−0.001(3)	−0.003(3)
C10	0.050(4)	0.110(5)	0.040(3)	0.042(4)	0.012(3)	0.027(3)
C11	0.030(2)	0.030(2)	0.037(2)	0.006(2)	0.005(2)	0.002(2)
C12	0.037(3)	0.045(3)	0.042(2)	0.008(2)	0.009(2)	0.012(2)
C13	0.030(3)	0.061(3)	0.050(2)	0.008(2)	0.006(2)	0.020(2)
C14	0.034(3)	0.061(3)	0.046(2)	0.017(2)	−0.001(2)	0.016(2)
C15	0.043(3)	0.045(3)	0.041(2)	0.012(2)	0.007(2)	0.013(2)
C16	0.039(3)	0.033(3)	0.033(2)	0.012(2)	0.008(2)	0.002(2)
C17	0.051(3)	0.028(2)	0.035(2)	0.008(2)	0.010(2)	0.006(2)
C18	0.051(3)	0.028(2)	0.037(2)	−0.002(2)	0.010(2)	0.001(2)
C19	0.037(2)	0.025(2)	0.033(2)	0.000(2)	0.007(2)	0.001(2)
C20	0.037(2)	0.024(2)	0.034(2)	−0.000(2)	0.010(2)	−0.000(2)
C21	0.036(3)	0.032(3)	0.038(2)	−0.008(2)	0.001(2)	0.007(2)
C22	0.043(3)	0.036(3)	0.034(2)	−0.005(2)	0.000(2)	0.004(2)
C23	0.041(3)	0.026(2)	0.036(2)	−0.006(2)	0.003(2)	−0.003(2)
C24	0.037(3)	0.020(2)	0.040(2)	−0.002(2)	0.007(2)	−0.001(2)
C25	0.042(3)	0.029(2)	0.047(2)	−0.004(2)	0.009(2)	0.003(2)
C26	0.043(3)	0.030(2)	0.054(3)	−0.004(2)	0.009(2)	−0.005(2)
C27	0.035(3)	0.024(2)	0.044(2)	−0.003(2)	0.003(2)	−0.002(2)
C28	0.050(3)	0.027(2)	0.042(2)	0.003(2)	0.002(2)	−0.004(2)
C29	0.033(2)	0.031(2)	0.039(2)	0.002(2)	−0.003(2)	0.003(2)
C30	0.037(3)	0.027(2)	0.051(2)	0.001(2)	−0.004(2)	−0.005(2)
C31	0.033(3)	0.033(3)	0.055(2)	0.002(2)	0.001(2)	−0.009(2)
C32	0.036(3)	0.038(3)	0.057(3)	0.001(2)	−0.001(2)	−0.003(2)
C33	0.041(3)	0.059(3)	0.042(2)	−0.017(2)	0.003(2)	0.001(2)
C34	0.059(4)	0.094(4)	0.079(3)	−0.038(3)	−0.030(3)	0.046(3)
C35	0.081(4)	0.216(7)	0.057(3)	−0.086(5)	−0.020(3)	0.019(4)
C36	0.042(3)	0.049(3)	0.177(6)	−0.001(3)	−0.024(4)	0.009(4)
C37	0.056(3)	0.039(3)	0.054(3)	−0.011(2)	−0.016(2)	0.005(2)

The general temperature factor expression:
$\exp(-2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2a^*b^*U_{12}hk+2a^*c^*U_{13}hl+2b^*c^*U_{23}kl))$

Table 3. Herbicidal activities of **1**-**4** (120 gai/10a)11)

	1	**2**	**3**	**4**
Digitaria ciliaris (Retz.) Koel	0	0	0	0
Setaria viridis Beauv.	40	0	50	0
Amaranthus blitum L.	0	0	60	0
Polygonum longisetum	0	0	0	0

The single crystals of **4** were obtained from the mixtures of methanol and $CHCl_3$ solution of **4**. A molecular view of **4** was shown in Fig. 2.

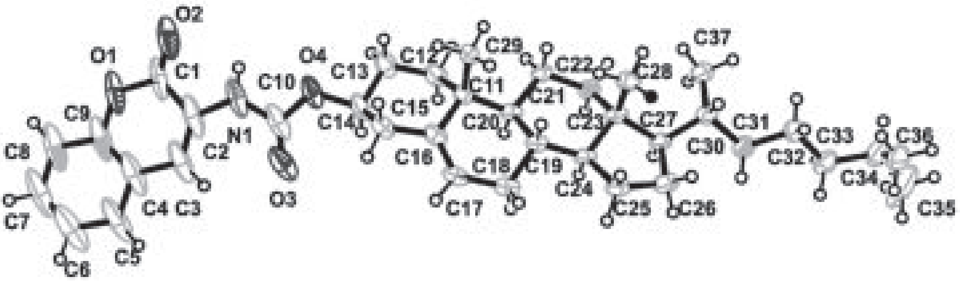


Fig. 2. An ORTEP drawing of **4** showing 50% probability displacement ellipsoids.

The C-C and C-O bond lengths of coumarin ring system agree with those coumarin, as shown in Table 4. The carbamate plane (refined by N1/C10/O3/O4) makes angles of 12.4(2)° and 49.5(1)° with the coumarin ring systems (refined by C1—C9/O1/O2) and the cyclopentanoperhydrophenanthrene least-squares plane (refined by C11—C27), respectively. The angle of the carbamate and coumarin planes is close to those [8.16(5)°16), 5.21(3)°17), 7.7(1)°17)] of t-butyl coumarin-3-carbamate (**1**), phenyl coumarin-3-carbamate (**2**), and testosterone derivative (**3**). The cyclohexane parts of **4** have chair conformations (C11—C12—C13—C14 −59.2(4)°, C12—C13—C14—C15 59.0(4)°, C13—C14—C15—C16 −54.5(4)°, C14—C15—C16—C11 51.0(4)°, C12—C11—C16—C15 −47.7(4)°, C16—C11—C12—C13 51.2(4)°, C11—C16—C17—C18 −0.3(5)°, C16—C17—C18—C19 13.9(5)°, C17—C18—C19—C20 −42.9(4)°, C18—C19—C20—C11 61.8(4)°, C16—C11—C20—C19 −47.7(4)°, C20—C11—C16—C17 16.9(4)°, C19—C20—C21—C22 48.6(4)°, C20—C21—C22—C23 −55.6(4)°, C21—C22—C23—C24 58.2(4)°, C22—C23—C24—C19 −60.3(4)°, C20—C19—C24—C23 54.9(4)°, C24—C19—C20—C21 −46.5(4)°). The molecular length of the compound (**4**) is 25.134(8) Å for the C7···C35 distance. There is an intramolecular N—H···O hydrogen bond in **4** as shown in Table 5.

There are some C—H···O hydrogen bonds in **4** as shown in Fig. 3 and Table 5. The C—H···O distances are close to this type of interaction (H···O: 2.5—2.7 Å).9,15,17,25-27) Some intermolecular C-H···π interactions are observed in **1** as shown in Fig. 3 and Table 5. The distance between atom

Table 4-1. Selected geometric parameters (Å, °)

O1—C1	1.361(7)	O1—C9	1.386(8)
O2—C1	1.204(8)	O3—C10	1.217(8)
O4—C10	1.349(7)	O4—C14	1.460(5)
N1—C2	1.402(7)	N1—C10	1.362(7)
C1—C2	1.485(8)	C2—C3	1.351(9)
C3—C4	1.452(7)	C4—C5	1.412(9)
C4—C9	1.399(9)	C5—C6	1.380(8)
C6—C7	1.358(10)	C7—C8	1.394(10)
C8—C9	1.385(8)	C11—C12	1.547(5)
C11—C16	1.531(5)	C11—C20	1.547(5)
C11—C29	1.551(5)	C12—C13	1.517(5)
C13—C14	1.515(6)	C14—C15	1.530(5)
C15—C16	1.519(5)	C16—C17	1.332(5)
C17—C18	1.491(5)	C18—C19	1.531(5)
C19—C20	1.536(5)	C19—C24	1.521(5)
C20—C21	1.546(5)	C21—C22	1.535(5)
C22—C23	1.531(5)	C23—C24	1.548(5)
C23—C27	1.555(5)	C23—C28	1.539(5)
C24—C25	1.528(5)	C25—C26	1.533(5)
C26—C27	1.568(5)	C27—C30	1.541(5)
C30—C31	1.539(5)	C30—C37	1.524(5)
C31—C32	1.526(5)	C32—C33	1.515(6)
C33—C34	1.521(6)	C34—C35	1.536(8)
C34—C36	1.506(7)		
C1—O1—C9	123.0(5)	C10—O4—C14	117.5(4)
C2—N1—C10	126.5(5)	O1—C1—O2	119.8(6)
O1—C1—C2	116.6(5)	O2—C1—C2	123.6(5)
N1—C2—C1	111.0(5)	N1—C2—C3	127.1(5)
C1—C2—C3	121.9(5)	C2—C3—C4	118.8(5)
C3—C4—C5	123.0(5)	C3—C4—C9	119.2(6)
C5—C4—C9	117.8(5)	C4—C5—C6	118.8(6)
C5—C6—C7	122.5(7)	C6—C7—C8	120.3(6)
C7—C8—C9	118.1(6)	O1—C9—C4	120.4(5)
O1—C9—C8	117.1(6)	C4—C9—C8	122.4(6)
O3—C10—O4	125.3(5)	O3—C10—N1	126.3(5)
O4—C10—N1	108.4(5)	C12—C11—C16	108.1(3)
C12—C11—C20	108.5(3)	C12—C11—C29	109.9(3)
C16—C11—C20	109.8(3)	C16—C11—C29	108.9(3)
C20—C11—C29	111.6(3)	C11—C12—C13	113.8(3)
C12—C13—C14	110.3(3)	O4—C14—C13	105.1(3)
O4—C14—C15	111.3(3)	C13—C14—C15	110.1(3)
C14—C15—C16	111.3(3)	C11—C16—C15	116.7(3)
C11—C16—C17	122.3(3)	C15—C16—C17	120.9(3)
C16—C17—C18	125.1(3)	C17—C18—C19	113.2(3)
C18—C19—C20	108.9(3)	C18—C19—C24	111.3(3)
C20—C19—C24	110.3(3)	C11—C20—C19	112.4(3)
C11—C20—C21	113.0(3)	C19—C20—C21	112.8(3)
C20—C21—C22	113.6(3)	C21—C22—C23	111.3(3)
C22—C23—C24	106.2(3)	C22—C23—C27	116.2(3)
C22—C23—C28	111.1(3)	C24—C23—C27	100.4(3)
C24—C23—C28	111.9(3)	C27—C23—C28	110.5(3)
C19—C24—C23	115.4(3)	C19—C24—C25	119.1(3)
C23—C24—C25	103.8(3)	C24—C25—C26	104.0(3)
C25—C26—C27	107.0(3)	C23—C27—C26	103.7(3)
C23—C27—C30	119.0(3)	C26—C27—C30	112.0(3)
C27—C30—C31	109.9(3)	C27—C30—C37	114.0(3)

Table 4‒2. Continued

C31—C30—C37	108.6(3)	C30—C31—C32	116.2(3)
C31—C32—C33	111.0(3)	C32—C33—C34	117.1(4)
C33—C34—C35	109.0(4)	C33—C34—C36	112.8(4)
C35—C34—C36	109.3(4)		
C1—O1—C9—C4	−1.8(6)	C1—O1—C9—C8	176.5(4)
C9—O1—C1—O2	−178.8(4)	C9—O1—C1—C2	0.7(6)
C10—O4—C14—C13	143.2(3)	C10—O4—C14—C15	−97.7(4)
C14—O4—C10—O3	15.4(6)	C14—O4—C10—N1	−163.9(3)
C2—N1—C10—O3	3.8(7)	C2—N1—C10—O4	−176.9(4)
C10—N1—C2—C1	−170.8(4)	C10—N1—C2—C3	9.3(7)
O1—C1—C2—N1	−178.8(4)	O1—C1—C2—C3	1.1(6)
O2—C1—C2—N1	0.7(7)	O2—C1—C2—C3	−179.4(4)
N1—C2—C3—C4	178.2(4)	C1—C2—C3—C4	−1.7(6)
C2—C3—C4—C5	−177.9(4)	C2—C3—C4—C9	0.6(6)
C3—C4—C5—C6	176.7(4)	C3—C4—C9—O1	1.2(6)
C3—C4—C9—C8	−177.0(4)	C5—C4—C9—O1	179.7(4)
C5—C4—C9—C8	1.5(7)	C9—C4—C5—C6	−1.8(6)
C4—C5—C6—C7	2.2(8)	C5—C6—C7—C8	−2.1(8)
C6—C7—C8—C9	1.7(7)	C7—C8—C9—O1	−179.7(4)
C7—C8—C9—C4	−1.4(7)	C12—C11—C16—C15	−47.7(4)
C12—C11—C16—C17	135.1(3)	C16—C11—C12—C13	51.2(4)
C12—C11—C20—C19	−165.7(3)	C12—C11—C20—C21	65.3(4)
C20—C11—C12—C13	170.2(3)	C29—C11—C12—C13	−67.5(4)
C16—C11—C20—C19	−47.7(4)	C16—C11—C20—C21	−176.8(3)
C20—C11—C16—C15	−165.8(3)	C20—C11—C16—C17	16.9(4)
C29—C11—C16—C15	71.7(4)	C29—C11—C16—C17	−105.6(4)
C29—C11—C20—C19	73.1(3)	C29—C11—C20—C21	−55.9(4)
C11—C12—C13—C14	−59.2(4)	C12—C13—C14—O4	179.0(3)
C12—C13—C14—C15	59.0(4)	O4—C14—C15—C16	−170.6(3)
C13—C14—C15—C16	−54.5(4)	C14—C15—C16—C11	51.0(4)
C14—C15—C16—C17	−131.7(4)	C11—C16—C17—C18	−0.3(5)
C15—C16—C17—C18	−177.4(3)	C16—C17—C18—C19	13.9(5)
C17—C18—C19—C20	−42.9(4)	C17—C18—C19—C24	−164.8(3)
C18—C19—C20—C11	61.8(4)	C18—C19—C20—C21	−169.0(3)
C18—C19—C24—C23	175.9(3)	C18—C19—C24—C25	−59.6(4)
C20—C19—C24—C23	54.9(4)	C20—C19—C24—C25	179.4(3)
C24—C19—C20—C11	−175.7(3)	C24—C19—C20—C21	−46.5(4)
C11—C20—C21—C22	177.5(3)	C19—C20—C21—C22	48.6(4)
C20—C21—C22—C23	−55.6(4)	C21—C22—C23—C24	58.2(4)
C21—C22—C23—C27	168.7(3)	C21—C22—C23—C28	−63.7(4)
C22—C23—C24—C19	−60.3(4)	C22—C23—C24—C25	167.6(3)
C22—C23—C27—C26	−151.5(3)	C22—C23—C27—C30	83.3(4)
C24—C23—C27—C26	−37.6(3)	C24—C23—C27—C30	−162.7(3)
C27—C23—C24—C19	178.4(3)	C27—C23—C24—C25	46.3(3)
C28—C23—C24—C19	61.2(4)	C28—C23—C24—C25	−71.0(3)
C28—C23—C27—C26	80.7(3)	C28—C23—C27—C30	−44.5(4)
C19—C24—C25—C26	−166.4(3)	C23—C24—C25—C26	−36.5(3)
C24—C25—C26—C27	12.2(4)	C25—C26—C27—C23	16.3(4)
C25—C26—C27—C30	145.8(3)	C23—C27—C30—C31	−175.3(3)
C23—C27—C30—C37	−53.0(4)	C26—C27—C30—C31	63.7(3)
C26—C27—C30—C37	−174.0(3)	C27—C30—C31—C32	−162.6(3)
C37—C30—C31—C32	72.0(4)	C30—C31—C32—C33	−174.5(3)
C31—C32—C33—C34	−174.9(3)	C32—C33—C34—C35	−176.5(3)
C32—C33—C34—C36	61.8(5)		

Table 5. N—H···O, C—H···π and C—H···O hydrogen bond geometry (Å, °)

D	H	A	D–H	H···A	D···A	D–H···A	Symmetry codes
N1	H1	O2	0.880	2.280	2.670(6)	107	
C5	H5	O2^{i}	0.950	2.704	3.599(7)	157	(i) x+2, y−1, −z
C8	H8	O3^{ii}	0.950	2.423	3.358(7)	169	(ii) x+1, y−2, −z
C17	H17	Cg1^{iii}	0.950	2.924	3.443	116	(iii) x+1, y, z
C29	H29A	C5^{iv}	0.980	2.870	3.750	150	(iv) x+1, y−1, −z
C35	H35C	C1^{v}	0.950	2.720	3.549(7)	143	(v) 3/2+x, 3/2−y, 1/4+z
C35	H35C	O1^{v}	0.950	2.654	3.411(6)	134	(v) 3/2+x, 3/2−y, 1/4+z

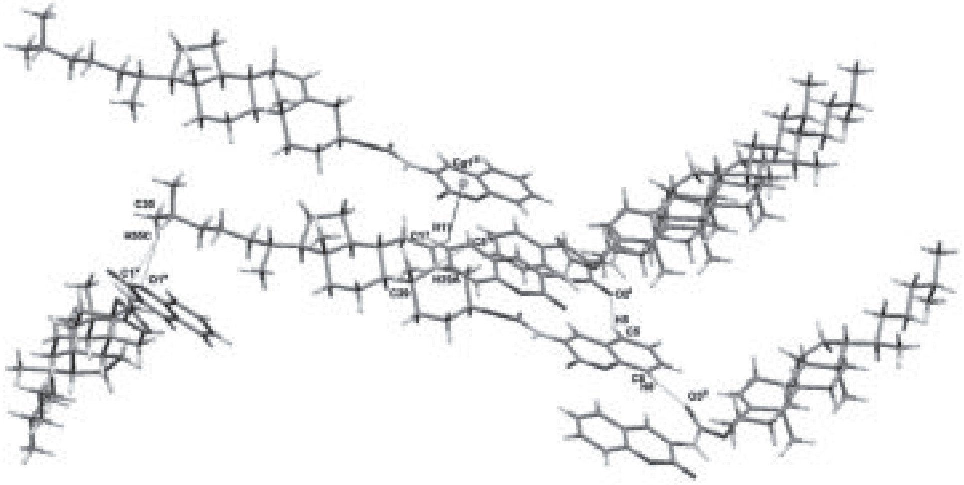


Fig. 3. Intermolecular C–H···π and C–H···O interactions of **4**. Symmetry codes: (i) x+2, y−1, −z, (ii) x+1, y−2, −z, (iii) x+1, y, z, (iv) x+1, y−1, −z, (v) 3/2+x, 3/2−y, 1/4+z. Cg1^{iii} is the centroid of C1^{iii}/O1^{iii}/C2^{iii}/C3^{iii}/C4^{iii}/C9^{iii}.

H17 and the centroid Cg1 (defined by C1^{iii}/O1^{iii}/C2^{iii}/C3^{iii}/C4^{iii}/C9^{iii}) (symmetry code: (iii) x+1, y, z) is 2.924 Å, which agree with this type interaction (H···C: 2.8—3.1 Å).[26,27]

In conclusion, the crystal structure of cholesteryl coumarin-3-carbamate (**4**) was elucidated by X-ray crystallographic analysis. Intermolecular C-H···π and C-H···O interactions help stabilized the crystal packing. There are no intermolecular N—H···O and N—H···π hydrogen bonds.

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