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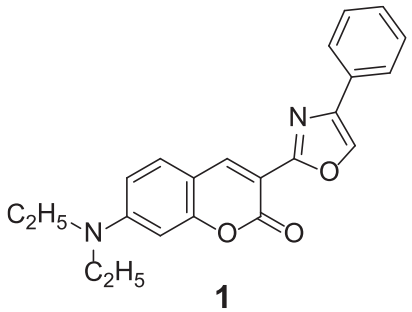
Crystal Structure of 7-(Diethylamino)-3-(4-phenyl-2-oxazolyl)coumarin

Kanji KUBO, Taisuke MATSUMOTO, and Haruko TAKECHI

Abstract — Structure of 7-(diethylamino)-3-(4-phenyl-2-oxazolyl)coumarin (**1**), $C_{22}H_{20}N_2O_3$, was determined by X-ray crystallographic analysis. It crystallizes in the space group $P2_1/c$ (#14) with cell parameters $a=16.215(3)$ Å, $b=12.887(3)$ Å, $c=16.994(4)$ Å, $\beta=93.5210(16)°$, $Z=8$, and $V=3544.4(13)$ Å^3. The structure of **1** contains two crystallographically independent molecules (**1a** and **1b**). with different conformations of the diethylamino groups. The two diethyl groups of diethylamino group of **1a** are *anti* with respect to one another. While those of **1b** are *syn* with respect to one another. The coumarin ring makes an angles of 30.7(1)° for **1a** and 12.8(1)° for **1b** with the oxazole rings, respectively. The crystals of the coumarin derivative (**1**) had intermolecular C—H···O, C—H···π, π···π interactions and O···C contact.

1. Introduction

Coumarin derivatives are a useful component for developing new materials, such as fluorescence materials and laser dyes; non-linear optical materials and reagents; photorefractive materials; photoresistors; intermediates for drug synthesis; analytical reagents, *etc.*[1] Although the fluorescence of the coumarin, itself, is weak, the introduction of a substituent group into coumarin increases the fluorescence intensity. Recently, we reported the synthesis and fluorescence properties of 7-(diethylamino)coumarin derivatives as fluorophores accessible for analytical purposes in the fields of analytical and biological chemistry.[2] The crystal structures of 7-(diethylamino)coumarin,[3] 7-diethylamino-3-dimethylaminocoumarin,[4] methyl 4-(7-diethylamino-2-oxo-*2H*-1-benzopyran-3-yl)benzoate,[5] cholesteryl 4-(7-diethylamino-2-oxo-*2H*-1-benzopyran-3-yl) benzoate,[6] 7-(diethylamino)-3-phenylcoumarin,[7] methyl 4-(7-diethylamino-2-oxo-*2H*-1-benzopyran-3-yl)benzoate,[7] 7-(diethylamino)-3-(oxazol-5-yl)coumarin,[8] 7-(dimethylamino)-3-(2-oxazoly) coumarin,[9] and 7-(diethylamino)coumarin-3-carboxylic acid hydrazide[10] have been reported. While, we reported the synthesis and property of 7-(diethylamino)-3-(4-phenyl-2-oxazolyl)coumarin (**1**, Fig. 1) as an organic fluorophore.[2] However, the crystal structure of **1** has not been reported. We now



1

Fig. 1. Chemical structure of 7-(diethylamino)-3-(4-phenyl-2-oxazolyl)coumarin (**1**).

report on the crystal structure of **1** with the aim to contribute to a deeper understanding of the substituent effect at the 3-position of 7-(diethylamino) coumarin on the structure and crystal packing.

2. Experimental

2.1. Analysis

The melting points were measured with a Yanagimoto Micro Melting Point Apparatus and are uncorrected. The NMR spectra were recorded using JEOL Lambda 400 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. Fluorescence spectra were measured using a JASCO FP-6500 spectrofluorometer.

2.2. Material

7-(Diethylamino)-3-(4-phenyl-2-oxazolyl) coumarin (**1**) was synthesized by the reaction of 7-(diethylamino)coumarin-3-calbaldehyde and bromoacetophenone in DMF as reported in a previous paper.[3] The spectral data of **1** are as follows: mp 158.5–160°C, ^{1}H NMR ($CDCl_3$) δ 1.24 (6H, *t*, J=7.2 Hz), 3.45 (4H, *q*, J=7.2 Hz), 6.54 (1H, *d*, J=2.4 Hz), 6.62 (1H, *dd*, J=9.1, 2.4 Hz), 7.3 (1H, *m*), 7.4 (3H, *m*), 8.03 (1H, *s*), and 8.54 (1H, *s*).

2.3. Data Collection

A red prism crystal of $C_{22}H_{20}N_2O_3$ having approximate dimensions of 0.17×0.14×0.07 mm was mounted on a glass fiber. All measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα radiation. Indexing was performed from 0 images that were exposed for 0 seconds. The crystal-to-detector distance was 44.93 mm. Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a=16.215(3) Å, b=12.887(3) Å, c=16.994(4) Å, β=93.5210(16)°, For Z=8 and $F.W.$=360.41, the calculated density is 1.351 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: $P2_1/c$ (#14).

The data were collected at a temperature of 150±1K to a maximum 2θ value of 55.0°. A total of 1080 oscillation images were collected. A sweep of data was done using ω scans from −110.0 to 70.0° in 0.5° step, at χ=45.0° and ϕ=0.0°. The exposure rate was 20.0 [sec./°]. The detector swing angle was −20.08°. A second sweep was performed using ω scans from −110.0 to 70.0° in 0.5° step, at χ=45.0° and ϕ=90.0°. The exposure rate was 20.0 [sec./°]. The detector swing angle was −20.08°. Another sweep was performed using ω scans from −110.0 to 70.0° in 0.5° step, at χ=45.0° and ϕ=180.0°. The exposure rate was 20.0 [sec./°]. The detector swing angle was −20.08°. The crystal-to-detector distance was 44.93 mm. Readout was performed in the 0.547 mm pixel mode.

2.4. Data Reduction

Of the 42341 reflections that were collected, 8107 were unique (R_{int}=0.055); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku). Net intensities and sigmas were derived as follows: $F^2=[\Sigma(P_i-mB_{ave})]\cdot Lp^{-1}$

where P_i is the value in counts of the ith pixel

m is the number of pixels in the integration area

B_{ave} is the background average

Lp is the Lorentz and polarization factor

$B_{ave}=\Sigma(B_j)/n$

where n is the number of pixels in the background area

B_j is the value of the j^{th} pixel in counts

$\sigma^2(F^2_{hkl})=[(\Sigma P_i)+m((\Sigma(B_{ave}-B_j)^2)/(n-1))]\cdot Lp\cdot errmul+(erradd\cdot F^2)^2$

where erradd=0.00

errmul=1.00

The linear absorption coefficient, μ, for Mo-Kα radiation is 0.907 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.927 to 0.994. The data were corrected for Lorentz and polarization effects.

2.5. Structure Solution and Refinement

The structure was solved by direct methods[11] and expanded using Fourier techniques[12]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding

model. The final cycle of full-matrix least-squares refinement on F^2 was based on 8107 observed reflections and 488 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of: $R_1=\Sigma\|F_0|-|F_c\|/\Sigma|F_0|=0.1047$, $wR_2=[\Sigma(w(F_0^2-F_c^2)^2)/\Sigma w(F_0^2)^2]^{1/2}=0.2522$. 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: N_o=number of observations, N_v=number of variables) was 1.18. A Sheldrick weighting scheme was used. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.32 and −0.50 e^-/A^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[12] Anomalous dispersion effects were included in F_{calc}[13]; the values for Δf′ and Δf″ were those of Creagh and McAuley[14] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[15] All calculations were performed using the *CrystalStructure3.8*[16] crystallographic software package except for refinement, which was performed using *SHELXL97*[17] Fractional atomic coordinates and equivalent isotropic displacement parameters were shown in Table 1. Anisotropic displacement parameters were shown in Table 2.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC1939826 for **1**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: + 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

3. Result & Discussion

7-(Diethylamino)-3-(4-phenyl-2-oxazolyl)coumarin (**1**) was synthesized by the reaction of 7-(diethylamino)coumarin-3-calbaldehyde and bromoacetophenone as reported in a previous paper.[3] 7-(Diethylamino)-3-(4-phenyl-2-oxazolyl)coumarin (**1**) gave strong emission band at 488 nm in ethanol solution when excited at428 nm. However 7-(diethylamino)-3-(4-phenyl-2-oxazolyl)coumarin (**1**) had no fluorescence in solid state.

Single crystals of **1** were obtained from the mixtures of ethyl acetate and chloroform (1:1 *v*/*v*). The data-collection and refinement parameters are listed in Table 3.

All C-bound H atoms were positioned with the idealized geometry and were refined to be isotropic (U_{iso}(H)=1.2U_{eq}(C)) using a riding model with C—H=0.95 Å for aromatic H atoms, C—H=0.98 Å for methyl H atoms, and C—H=0.99 Å for methylene H atoms. The selected bond distances and torsion angles are collected in Table 3. An ORTEP drawing of **1** was shown in Fig. 2.

The structure of **1** contains two crystallographically independent molecules (**1a** and **1b**) with

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

atom	x	y	z	B_{eq}
O1	0.72171(13)	0.40439(17)	0.34933(13)	2.50(3)
O2	0.84080(13)	0.48172(17)	0.37753(14)	2.77(4)
O3	0.93597(13)	0.40340(17)	0.50945(13)	2.57(4)
O4	0.77862(14)	0.08975(17)	0.64687(15)	2.95(4)
O5	0.67709(16)	0.00492(19)	0.58439(17)	3.87(5)
O6	0.52540(13)	0.10057(17)	0.55776(13)	2.53(3)
N1	0.45330(15)	0.2730(2)	0.28638(16)	2.56(4)
N2	0.94186(15)	0.2313(2)	0.50124(16)	2.39(4)
N3	1.01877(19)	0.2551(2)	0.7636(2)	3.65(6)
N4	0.52667(16)	0.2733(2)	0.56659(15)	2.45(4)
C1	0.79848(18)	0.4072(2)	0.38926(18)	2.26(5)
C2	0.81974(18)	0.3184(2)	0.43936(18)	2.29(5)
C3	0.76687(18)	0.2361(2)	0.44294(18)	2.19(4)
C4	0.68826(18)	0.2364(2)	0.40133(18)	2.24(5)
C5	0.62844(19)	0.1579(2)	0.40327(19)	2.48(5)
C6	0.5522(2)	0.1676(2)	0.36507(19)	2.56(5)
C7	0.53008(18)	0.2598(2)	0.32228(18)	2.34(5)
C8	0.59032(18)	0.3374(2)	0.31875(18)	2.35(5)
C9	0.66651(18)	0.3244(2)	0.35635(18)	2.23(5)
C10	0.4334(2)	0.3641(2)	0.23793(19)	2.82(5)
C11	0.4004(2)	0.4537(2)	0.2848(2)	3.49(6)
C12	0.3860(2)	0.1993(2)	0.2953(2)	2.95(6)
C13	0.3808(2)	0.1184(3)	0.2315(2)	4.14(7)
C14	0.89969(18)	0.3140(2)	0.48244(18)	2.22(4)
C15	1.01262(18)	0.2673(2)	0.54337(18)	2.26(5)
C16	1.00910(19)	0.3715(2)	0.54797(19)	2.46(5)
C17	1.07889(18)	0.1972(2)	0.57131(17)	2.35(5)
C18	1.0680(2)	0.0903(2)	0.56537(19)	2.73(5)
C19	1.1310(2)	0.0229(2)	0.5887(2)	3.42(6)
C20	1.2061(2)	0.0611(3)	0.6199(2)	3.51(6)
C21	1.2165(2)	0.1675(3)	0.6270(2)	3.37(6)
C22	1.15429(19)	0.2355(2)	0.6024(2)	2.75(5)
C23	0.6988(2)	0.0865(2)	0.6138(2)	2.68(5)
C24	0.65150(18)	0.1813(2)	0.61642(18)	2.30(5)
C25	0.68633(19)	0.2680(2)	0.65035(18)	2.51(5)
C26	0.76891(19)	0.2688(2)	0.68271(18)	2.38(5)
C27	0.8096(2)	0.3554(2)	0.7175(2)	2.87(5)
C28	0.8905(2)	0.3503(2)	0.7451(2)	3.06(6)
C29	0.9367(2)	0.2581(2)	0.7397(2)	2.86(5)
C30	0.8955(2)	0.1699(2)	0.7086(2)	2.79(5)
C31	0.81432(19)	0.1777(2)	0.67988(18)	2.33(5)
C32	1.0631(2)	0.1567(2)	0.7737(2)	2.99(6)
C33	1.0406(2)	0.0964(3)	0.8447(2)	3.33(6)
C34	1.0709(3)	0.3525(3)	0.7786(2)	4.70(8)
C35	1.0780(3)	0.3737(3)	0.8637(2)	5.12(9)
C36	0.56797(19)	0.1880(2)	0.58004(18)	2.37(5)
C37	0.45029(18)	0.2416(2)	0.53142(18)	2.29(5)
C38	0.45068(19)	0.1367(2)	0.52660(18)	2.44(5)
C39	0.38750(18)	0.3177(2)	0.50541(17)	2.35(5)
C40	0.4027(2)	0.4232(2)	0.51321(19)	2.67(5)
C41	0.3442(2)	0.4962(2)	0.4881(2)	3.08(6)
C42	0.2677(2)	0.4644(3)	0.4554(2)	3.27(6)
C43	0.2516(2)	0.3588(3)	0.4481(2)	3.12(6)
C44	0.3105(2)	0.2862(2)	0.4725(2)	2.86(5)

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

Table 2. Anisotropic displacement parameters (Å^2)

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0271(10)	0.0318(11)	0.0354(11)	−0.0020(9)	−0.0043(8)	0.0057(9)
O2	0.0268(11)	0.0338(12)	0.0440(13)	−0.0053(9)	−0.0041(9)	0.0057(10)
O3	0.0305(11)	0.0295(11)	0.0363(12)	0.0000(9)	−0.0096(9)	−0.0015(9)
O4	0.0340(12)	0.0280(11)	0.0481(14)	0.0030(9)	−0.0123(10)	−0.0056(10)
O5	0.0464(14)	0.0308(12)	0.0668(18)	−0.0006(11)	−0.0221(12)	−0.0094(12)
O6	0.0309(11)	0.0312(11)	0.0335(11)	−0.0060(9)	−0.0027(9)	−0.0001(9)
N1	0.0244(12)	0.0349(14)	0.0369(14)	−0.0022(11)	−0.0053(10)	−0.0018(11)
N2	0.0262(12)	0.0315(13)	0.0325(13)	0.0006(10)	−0.0039(10)	0.0006(11)
N3	0.0384(16)	0.0359(16)	0.062(2)	0.0000(13)	−0.0155(14)	−0.0122(14)
N4	0.0275(13)	0.0341(14)	0.0313(13)	−0.0037(11)	0.0006(10)	−0.0017(11)
C1	0.0204(13)	0.0329(16)	0.0318(15)	0.0014(12)	−0.0026(11)	−0.0034(12)
C2	0.0245(14)	0.0337(16)	0.0288(14)	0.0017(12)	0.0003(11)	−0.0023(12)
C3	0.0292(15)	0.0260(14)	0.0277(14)	0.0018(12)	−0.0009(11)	−0.0015(11)
C4	0.0274(14)	0.0288(15)	0.0286(15)	0.0020(12)	0.0005(11)	−0.0026(12)
C5	0.0320(16)	0.0308(15)	0.0314(15)	0.0018(13)	0.0021(12)	0.0004(12)
C6	0.0313(15)	0.0344(16)	0.0314(15)	−0.0043(13)	0.0012(12)	−0.0040(12)
C7	0.0266(14)	0.0362(16)	0.0257(14)	0.0016(12)	−0.0007(11)	−0.0066(12)
C8	0.0266(14)	0.0321(15)	0.0301(15)	0.0005(12)	−0.0020(11)	0.0029(12)
C9	0.0276(14)	0.0294(15)	0.0280(14)	−0.0009(12)	0.0022(11)	−0.0043(12)
C10	0.0267(15)	0.049(2)	0.0312(16)	−0.0013(14)	−0.0030(12)	0.0010(14)
C11	0.0401(19)	0.047(2)	0.046(2)	0.0097(16)	0.0061(15)	0.0068(16)
C12	0.0287(16)	0.0445(19)	0.0383(18)	−0.0038(14)	−0.0026(13)	−0.0033(15)
C13	0.052(2)	0.047(2)	0.058(2)	−0.0075(18)	−0.0043(18)	−0.0169(19)
C14	0.0266(14)	0.0281(15)	0.0292(15)	0.0001(12)	−0.0015(11)	−0.0010(12)
C15	0.0262(14)	0.0336(16)	0.0254(14)	−0.0033(12)	−0.0037(11)	0.0010(12)
C16	0.0279(15)	0.0311(16)	0.0336(16)	0.0016(12)	−0.0064(12)	0.0019(12)
C17	0.0279(15)	0.0379(17)	0.0229(14)	0.0037(12)	−0.0031(11)	0.0027(12)
C18	0.0375(17)	0.0333(17)	0.0324(16)	0.0022(14)	−0.0036(13)	−0.0010(13)
C19	0.052(2)	0.0363(18)	0.0414(19)	0.0115(16)	0.0010(16)	−0.0011(15)
C20	0.0360(18)	0.052(2)	0.045(2)	0.0195(16)	0.0007(15)	0.0094(17)
C21	0.0275(16)	0.057(2)	0.0431(19)	0.0062(15)	−0.0041(14)	0.0060(17)
C22	0.0291(16)	0.0392(18)	0.0356(17)	−0.0012(13)	−0.0028(13)	0.0053(14)
C23	0.0305(16)	0.0320(17)	0.0380(17)	−0.0008(13)	−0.0082(13)	0.0021(13)
C24	0.0274(15)	0.0328(16)	0.0268(14)	−0.0023(12)	−0.0030(11)	0.0004(12)
C25	0.0333(16)	0.0343(16)	0.0273(15)	0.0038(13)	−0.0027(12)	−0.0014(12)
C26	0.0305(15)	0.0323(16)	0.0268(14)	−0.0017(12)	−0.0045(11)	−0.0033(12)
C27	0.0415(18)	0.0277(16)	0.0386(17)	0.0018(14)	−0.0084(14)	−0.0042(13)
C28	0.0403(18)	0.0337(17)	0.0405(18)	−0.0001(14)	−0.0116(14)	−0.0057(14)
C29	0.0342(16)	0.0305(16)	0.0424(18)	−0.0007(13)	−0.0103(14)	−0.0044(13)
C30	0.0370(17)	0.0301(16)	0.0372(17)	0.0027(13)	−0.0101(13)	−0.0022(13)
C31	0.0334(16)	0.0246(15)	0.0296(15)	−0.0050(12)	−0.0062(12)	−0.0020(11)
C32	0.0337(17)	0.0425(19)	0.0365(17)	0.0043(14)	−0.0051(13)	−0.0054(14)
C33	0.0311(17)	0.058(2)	0.0365(18)	−0.0026(16)	−0.0043(13)	−0.0040(16)
C34	0.072(2)	0.054(2)	0.053(2)	0.006(2)	0.001(2)	0.006(2)
C35	0.072(3)	0.063(2)	0.059(2)	0.006(2)	−0.003(2)	0.010(2)
C36	0.0308(15)	0.0293(15)	0.0298(15)	−0.0052(12)	0.0009(12)	−0.0006(12)
C37	0.0258(14)	0.0360(16)	0.0250(14)	−0.0024(12)	0.0004(11)	−0.0021(12)
C38	0.0259(14)	0.0367(17)	0.0294(15)	−0.0050(12)	−0.0040(11)	−0.0009(13)
C39	0.0241(14)	0.0398(17)	0.0252(14)	−0.0003(12)	0.0016(11)	−0.0026(12)
C40	0.0334(16)	0.0376(18)	0.0301(15)	−0.0024(13)	−0.0006(12)	−0.0019(13)
C41	0.0452(19)	0.0375(18)	0.0343(17)	0.0077(15)	0.0031(14)	−0.0037(14)
C42	0.0370(18)	0.051(2)	0.0365(18)	0.0125(16)	0.0031(14)	−0.0017(15)
C43	0.0283(16)	0.054(2)	0.0363(17)	−0.0002(15)	−0.0010(13)	−0.0003(15)
C44	0.0331(17)	0.0407(18)	0.0349(17)	−0.0017(14)	0.0018(13)	−0.0003(14)

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. Crystal and experimental data

Chemical formula: $C_{22}H_{20}N_2O_3$	
Formula weight＝360.41	
T＝150K	
Crystal system: Monoclinic	Space group: $P2_1/c$
a＝16.215(3) Å	
b＝12.887(3) Å	β＝93.5210(16)°
c＝16.994(4) Å	
V＝3544.4(13) Å^3	Z＝8
D_x＝1.351 g/cm^3	
Radiation: Mo K_α (λ＝0.71070 Å) graphite monochromated	
μ(Mo K_α)＝0.907 cm^{-1}	F(000)＝1520.00
Crystal size＝0.17×0.14×0.07 mm^3	
$2\theta_{max}$ ＝55.0° with Mo K_α	
Data/Restraints/Parameters＝8107/0/488	
R indices [$I \geq 2\sigma(I)$]: $R1$＝0.1047	
R indices (all data): $R1$＝0.1259, $wR2$＝0.2522	
Goodness-of-fit on F^2＝1.175	
$(\Delta/\sigma)_{max}$＝0.001	
$(\Delta\rho)_{max}$＝1.32 eÅ^{-3}	$(\Delta\rho)_{min}$＝−0.50 eÅ^{-3}
Measurement: Rigaku Saturn CCD diffractometer	
Program System: *CrystalStructure 3.8*	
Data collection & cell refinement program: *CrystalStructure 3.8*	
Data reduction program: *CrystalStructure 3.8*	
Structure solving program: *SIR92*	
Structure refinement program: *SHELXL97*	

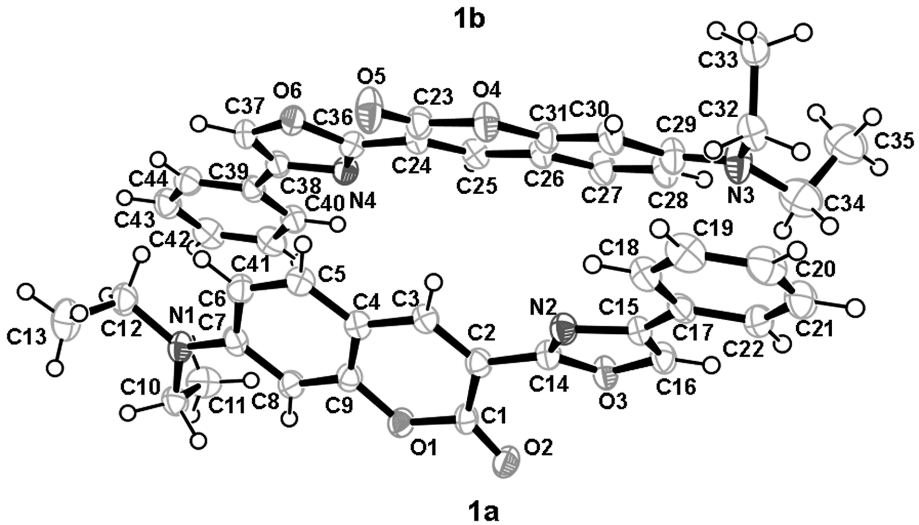


Fig. 2. An ORTEP drawing of **1** showing 50% probability displacement ellipsoids.

different conformations of the diethylamino groups. The two diethyl groups of diethylamino group of **1a** are *anti* with respect to one another. While the two diethyl groups of diethylamino group of **1b** are *syn* with respect to one another.

As shown in Table 4, the C-C and C-O bond lengths and angles in the coumarin ring system in both molecules are normal and are in good agreement with those observed in 7-(diethylamino) coumarin,[3] 7-diethylamino-3-dimethylaminocoumarin,[4] methyl 4-(7-diethylamino-2-oxo-*2H*-1-benzopyran-3-yl)benzoate,[5] cholesteryl 4-(7-diethylamino-2-oxo-*2H*-1-benzopyran-3-yl)benzoate,[6] 7-(diethylamino)-3-phenylcoumarin,[7] methyl 4-(7-diethylamino-2-oxo-*2H*-1-benzopyran-3-yl) benzoate,[7] 7-(diethylamino)-3-(oxazol-5-yl)coumarin,[8] and 7-(dimethylamino)-3-(2-oxazoly)coumarin[9]. The N1-C7 and N3-C29 bond lengths are close to that of the value (1.355 Å)[19] observed for a Csp^2-Nsp^2 bond. This means that the diethyamino group substituted at the C7 position effects the conjugation system of coumarin. The respective deviations of each atom from the least-squares plane defined by atoms C7, C10, C12 and N1 are 0.004(1) Å, 0.004(1) Å, 0.004(1) Å, and −0.007(2) Å, respectively. While, those of each atom from the least-squares plane defined by atoms C29, C32, C34 and N3 are −0.005(1) Å, −0.004(1) Å, −0.007(2) Å, and 0.011(3) Å, respectively.

The coumarin rings (defined by O1/O2/C1/C2/C3/C4/C5/C6/C7/C8/C9 and O4/O5/C23/C24/C25/C26/C27/C28/C29/C30/C31) make angles of 30.7(1)° for **1a** and 12.8(1)° for **1b** with the oxazole rings (defined by N2/O3/C14/C15/C16 and N4/O6/C36/C37/C38), respectively. The dihedral angles between the oxazole rings and benzene rings (defined by C17/C18/C19/C20/C21/C22 and C39/C40/C41/C42/C43/C44) are 8.5(1)° for **1a** and 2.9(1)° for **1b**, respectively. The angle between the coumarin planes of two molecules (**1a** and **1b**) is 42.2(1)°.

There are some intermolecular C—H···O and C—H···π interactions (Figs. 3, 4, 5 and Table 5). The C—H···O distances are close to this type of interaction (H···O: 2.5—2.7 Å).[4–10] For the intermolecular C—H···π interactions, the H···C distances agree with the distance for this type of interaction (H···C: 2.8—3.1 Å).[4–9]

The Intermolecular π···π interactions are shown in Figs. 3, 4, and 5. The distances between the intermolecular coumarin planes are 3.240(4) Å for C5···C36 (Fig. 3) and 3.347(4) Å (Fig. 4) for C1···C42^{vi}, respectively (symmetry code: (vi) 1-x, 1-y, 1-z). The distances are within the range associated with π···π interactions (3.3–3.8 Å).[5,7,9,10]

There is an intermolecular O···C contact (Fig. 4). The O3···C16 distance is 3.204(3) Å, which is similar to the respective sums of the van der Waals radii (3.22 Å).[20]

In conclusion, the crystal structure of 7-(diethylamino)-3-(4-phenyl-2-oxazolyl)coumarin (**1**) was elucidated by X-ray crystallographic analysis. Intermolecular C—H···O, C—H···π, π···π interactions, and O···C contact help stabilized the crystal packing.

Table 4. Selected geometric parameters (Å,°)

O1-C1	1.381(3)	O1-C9	1.375(3)
O2-C1	1.204(3)	O3-C14	1.361(3)
O3-C16	1.381(3)	O4-C23	1.380(3)
O4-C31	1.376(3)	O5-C23	1.207(4)
O6-C36	1.363(3)	O6-C38	1.373(3)
N1-C7	1.363(3)	N1-C10	1.459(4)
N1-C12	1.461(4)	N2-C14	1.296(3)
N2-C15	1.394(3)	N3-C29	1.368(4)
N3-C32	1.463(4)	N3-C34	1.526(5)
N4-C36	1.300(4)	N4-C37	1.403(3)
C1-C2	1.455(4)	C2-C3	1.368(4)
C2-C14	1.450(4)	C3-C4	1.419(4)
C4-C5	1.404(4)	C4-C9	1.401(4)
C5-C6	1.367(4)	C6-C7	1.427(4)
C7-C8	1.402(4)	C8-C9	1.366(4)
C10-C11	1.518(5)	C12-C13	1.503(5)
C15-C16	1.347(4)	C15-C17	1.460(4)
C17-C18	1.392(4)	C17-C22	1.392(4)
C18-C19	1.381(5)	C19-C20	1.388(5)
C20-C21	1.386(5)	C21-C22	1.382(4)
C23-C24	1.445(4)	C24-C25	1.364(4)
C24-C36	1.456(4)	C25-C26	1.416(4)
C26-C27	1.408(4)	C26-C31	1.388(4)
C27-C28	1.367(4)	C28-C29	1.411(4)
C29-C30	1.405(4)	C30-C31	1.379(4)
C32-C33	1.500(5)	C34-C35	1.470(6)
C37-C38	1.355(4)	C37-C39	1.462(4)
C39-C40	1.387(4)	C39-C44	1.397(4)
C40-C41	1.386(4)	C41-C42	1.390(4)
C42-C43	1.389(5)	C43-C44	1.382(4)
C1-O1-C9	123.3(2)	C14-O3-C16	104.4(2)
C23-O4-C31	123.5(2)	C36-O6-C38	104.3(2)
C7-N1-C10	121.1(2)	C7-N1-C12	122.7(2)
C10-N1-C12	116.2(2)	C14-N2-C15	104.9(2)
C29-N3-C32	121.4(2)	C29-N3-C34	123.0(3)
C32-N3-C34	115.5(2)	C36-N4-C37	105.1(2)
O1-C1-O2	116.4(2)	O1-C1-C2	116.2(2)
O2-C1-C2	127.4(2)	C1-C2-C3	120.6(2)
C1-C2-C14	119.9(2)	C3-C2-C14	119.4(2)
C2-C3-C4	121.5(2)	C3-C4 C5	125.9(2)
C3-C4-C9	117.6(2)	C5-C4-C9	116.5(2)
C4-C5-C6	122.0(2)	C5-C6-C7	120.6(2)
N1-C7-C6	121.7(2)	N1-C7-C8	120.8(2)
C6-C7-C8	117.5(2)	C7-C8-C9	120.3(2)
O1-C9-C4	120.7(2)	O1-C9-C8	116.2(2)
C4-C9-C8	123.0(2)	N1-C10-C11	112.9(2)
N1-C12-C13	112.7(3)	O3-C14-N2	113.8(2)
O3-C14-C2	119.4(2)	N2-C14-C2	126.8(2)
N2-C15-C16	109.0(2)	N2-C15-C17	121.8(2)
C16-C15-C17	129.1(2)	O3-C16-C15	107.9(2)
C15-C17-C18	120.1(2)	C15-C17-C22	121.0(2)
C18-C17-C22	118.9(2)	C17-C18-C19	120.9(3)

C18-C19-C20	120.1(3)	C19-C20-C21	118.9(3)
C20-C21-C22	121.2(3)	C17-C22-C21	119.9(3)
O4-C23-O5	116.0(2)	O4-C23-C24	116.6(2)
O5-C23-C24	127.4(3)	C23-C24-C25	120.0(2)
C23-C24-C36	121.2(2)	C25-C24-C36	118.7(2)
C24-C25-C26	121.8(2)	C25-C26-C27	125.1(2)
C25-C26-C31	118.2(2)	C27-C26-C31	116.7(2)
C26-C27-C28	121.4(3)	C27-C28-C29	121.4(3)
N3-C29-C28	121.0(3)	N3-C29-C30	121.3(3)
C28-C29-C30	117.6(3)	C29-C30-C31	119.7(3)
O4-C31-C26	120.0(2)	O4-C31-C30	116.9(2)
C26-C31-C30	123.1(2)	N3-C32-C33	113.6(3)
N3-C34-C35	109.0(3)	O6-C36-N4	113.8(2)
O6-C36-C24	120.7(2)	N4-C36-C24	125.5(2)
N4-C37-C38	108.0(2)	N4-C37-C39	120.9(2)
C38-C37-C39	131.1(2)	O6-C38-C37	108.8(2)
C37-C39-C40	120.8(2)	C37-C39-C44	121.0(2)
C40-C39-C44	118.2(2)	C39-C40-C41	121.5(2)
C40-C41-C42	120.0(3)	C41-C42-C43	118.8(3)
C42-C43-C44	121.0(3)	C39-C44-C43	120.5(3)
C1-O1-C9-C4	−4.5(4)	C1-O1-C9-C8	174.2(2)
C9-O1-C1-O2	179.8(2)	C9-O1-C1-C2	1.2(4)
C14-O3-C16-C15	−0.8(3)	C16-O3-C14-N2	1.0(3)
C16-O3-C14-C2	179.1(2)	C23-O4-C31-C26	1.5(4)
C23-O4-C31-C30	−178.1(3)	C31-O4-C23-O5	177.2(3)
C31-O4-C23-C24	−1.3(4)	C36-O6-C38-C37	−0.4(3)
C38-O6-C36-N4	0.8(3)	C38-O6-C36-C24	179.9(2)
C7-N1-C10-C11	−90.0(3)	C10-N1-C7-C6	−175.4(2)
C10-N1-C7-C8	5.0(4)	C7-N1-C12-C13	−92.8(3)
C12-N1-C7-C6	6.2(4)	C12-N1-C7-C8	−173.4(2)
C10-N1-C12-C13	88.6(3)	C12-N1-C10-C11	88.5(3)
C14-N2-C15-C16	0.2(3)	C14-N2-C15-C17	−176.4(2)
C15-N2-C14-O3	−0.8(3)	C15-N2-C14-C2	−178.7(3)
C29-N3-C32-C33	−72.4(4)	C32-N3-C29-C28	167.2(3)
C32-N3-C29-C30	−13.1(5)	C29-N3-C34-C35	99.1(4)
C34-N3-C29-C28	−15.1(5)	C34-N3-C29-C30	164.6(3)
C32-N3-C34-C35	−83.1(4)	C34-N3-C32-C33	109.7(3)
C36-N4-C37-C38	0.5(3)	C36-N4-C37-C39	−178.1(2)
C37-N4-C36-O6	−0.8(3)	C37-N4-C36-C24	−179.9(2)
O1-C1-C2-C3	2.6(4)	O1-C1-C2-C14	179.0(2)
O2-C1-C2-C3	−175.8(3)	O2-C1-C2 C14	0.5(5)
C1-C2-C3-C4	−3.1(4)	C1-C2-C14-O3	33.2(4)
C1-C2-C14-N2	−149.0(3)	C3-C2-C14-O3	−150.4(2)
C3-C2-C14-N2	27.4(4)	C14-C2-C3-C4	−179.5(2)
C2-C3-C4-C5	−177.6(3)	C2-C3-C4-C9	−0.1(3)
C3-C4-C5-C6	175.9(3)	C3-C4-C9-O1	3.9(4)
C3-C4-C9-C8	−174.7(2)	C5-C4-C9-O1	−178.4(2)
C5-C4-C9-C8	3.0(4)	C9-C4-C5-C6	−1.6(4)
C4-C5-C6-C7	−0.9(5)	C5-C6-C7-N1	−177.3(3)
C5-C6-C7-C8	2.3(4)	N1-C7-C8-C9	178.6(2)
C6-C7-C8-C9	−1.0(4)	C7-C8-C9-O1	179.7(2)
C7-C8-C9-C4	−1.7(4)	N2-C15-C16-O3	0.4(3)
N2-C15-C17-C18	−8.5(4)	N2-C15-C17-C22	170.0(2)

C16-C15-C17-C18	175.7(3)	C16-C15-C17-C22	−5.8(5)
C17-C15-C16-O3	176.7(2)	C15-C17-C18-C19	177.6(3)
C15-C17-C22-C21	−178.8(3)	C18-C17-C22-C21	−0.3(4)
C22-C17-C18-C19	−0.9(4)	C17-C18-C19-C20	1.1(5)
C18-C19-C20-C21	−0.1(4)	C19-C20-C21-C22	−1.2(5)
C20-C21-C22-C17	1.4(5)	O4-C23-C24-C25	0.1(3)
O4-C23-C24-C36	177.1(2)	O5-C23-C24-C25	−178.2(3)
O5-C23-C24-C36	−1.2(5)	C23-C24-C25-C26	0.8(4)
C23-C24-C36-O6	14.4(4)	C23-C24-C36-N4	−166.6(3)
C25-C24-C36-O6	−168.5(2)	C25-C24-C36-N4	10.5(4)
C36-C24-C25-C26	−176.3(2)	C24-C25-C26-C27	179.0(3)
C24-C25-C26-C31	−0.6(4)	C25-C26-C27-C28	−177.8(3)
C25-C26-C31-O4	−0.5(4)	C25-C26-C31-C30	179.1(3)
C27-C26-C31-O4	179.8(2)	C27-C26-C31-C30	−0.5(4)
C31-C26-C27-C28	1.7(4)	C26-C27-C28-C29	0.2(4)
C27-C28-C29-N3	176.5(3)	C27-C28-C29-C30	−3.2(5)
N3-C29-C30-C31	−175.4(3)	C28-C29-C30-C31	4.3(5)
C29-C30-C31-O4	177.1(3)	C29-C30-C31-C26	−2.5(5)
N4-C37-C38-O6	−0.0(2)	N4-C37-C39-C40	1.5(4)
N4-C37-C39-C44	−178.1(2)	C38-C37-C39-C40	−176.7(3)
C38-C37-C39-C44	3.7(5)	C39-C37-C38-O6	178.4(3)
C37-C39-C40-C41	179.3(3)	C37-C39-C44-C43	−180.0(2)
C40-C39-C44-C43	0.4(4)	C44-C39-C40-C41	−1.1(4)
C39-C40-C41-C42	1.1(5)	C40-C41-C42-C43	−0.5(5)
C41-C42-C43-C44	−0.2(4)	C42-C43-C44-C39	0.2(4)

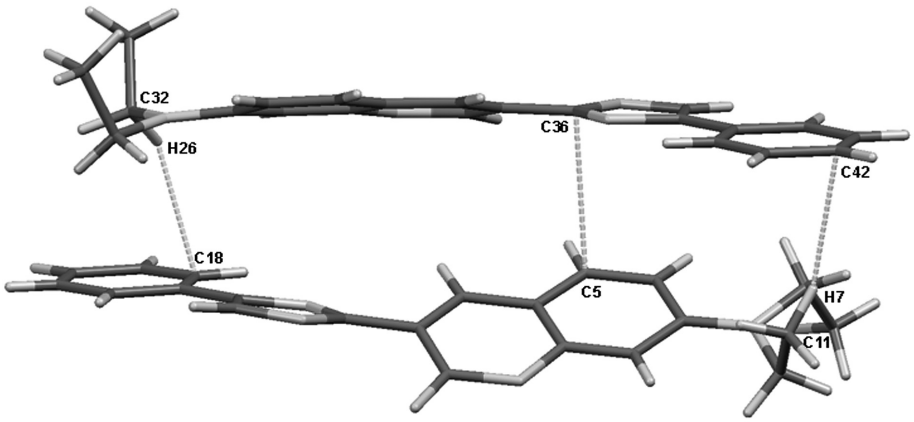


Fig. 3. Intermolecular C—H···π and π···π interactions in **1a** and **1b**.

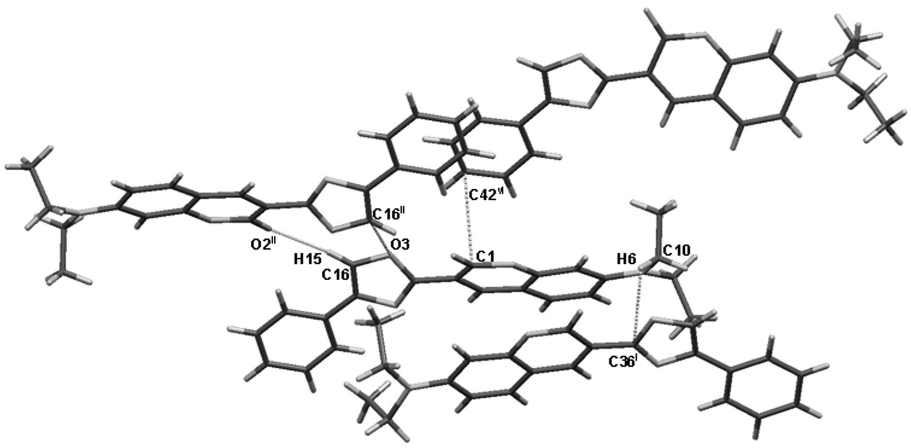


Fig. 4. Intermolecular C—H···π, C—H···O, and π···π interactions and C···O contact in **1a**.

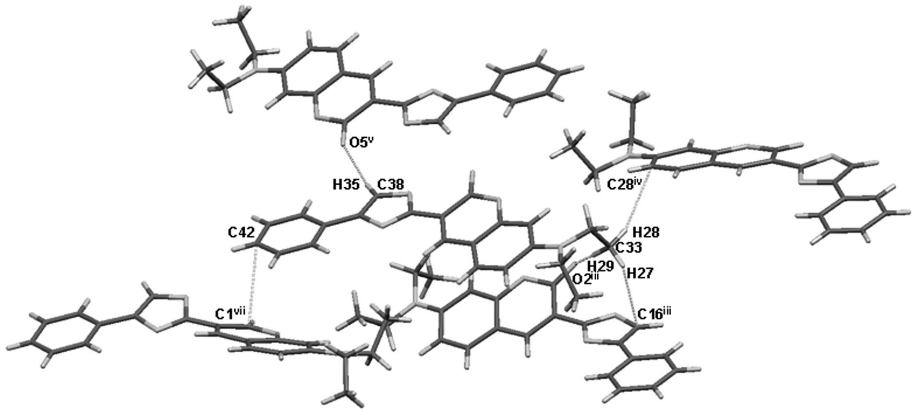


Fig. 5. Intermolecular C—H···π, C—H···O, and π···π interactions in **1b**.

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

D	H	A	D—H	H···A	D···A	D—H···A	Symmetry codes
C10	H6	C36^{i}	0.990	2.875	3.624(5)	133	(i) x, 1/2-y, z-1/2
C16	H15	O2^{ii}	0.950	2.330	3.275(3)	173	(ii) 2-x, 1-y, 1-z
C32	H26	C18	0.980	2.777	3.648(5)	147	
C33	H27	C16^{iii}	0.950	2.886	3.546(4)	126	(iii) x, 1/2-y, z + 1/2
C33	H28	C28^{iv}	0.950	2.812	3.721(5)	155	(iv) 2-x, y-1/2, 3/2-z
C33	H29	O2^{iii}	0.950	2.578	3.470(4)	151	(iii) x, 1/2-y, z + 1/2
C38	H35	O5^{v}	0.950	2.357	3.271(4)	160	(v) 1-x, -y, 1-z

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5. References and Notes

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