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Crystal Structure of 7-Diethylaminocoumarin-3-carboxylic Acid Hydrazide at 123 K

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Abstract — Structure of 7-diethylaminocoumarin-3-carboxylic acid hydrazide (**1**), $C_{14}H_{17}N_3O_3$, was determined by X-ray crystallographic analysis at 123 K. It crystallizes in the space group $P\bar{1}$ (#2) with cell parameters $a=9.2098(19)$ Å, $b=12.619(3)$ Å, $c=12.940(3)$ Å, $\alpha=94.734(15)°$, $\beta=109.987(14)°$, $\gamma=105.328(14)°$, $Z=4$, and $V=1338.0(5)$ Å^3. The structure of **1** contains two crystallographically independent molecules (**1a** and **1b**). The two molecules are almost planar. The crystals of the coumarin derivative (**1**) had intermolecular N—H⋯O, C—H⋯O, C—H⋯N, and $\pi\cdots\pi$ interactions.

1. Introduction

Fluorescence is highly sensitive to physicochemical environments. A variety of organic fluorophores have been widely used in many scientific fields, for example, as analytical tools such as fluorescence labeling reagents, fluorescence probes, fluorescence sensors, and laser dyes. Coumarin is a chemical compound found in many plants, notably in high concentration in the Tonka bean woodruff, and bison grass. 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-2*H*-1-benzopyran-3-yl)benzoate,5) cholesteryl 4-(7-diethylamino-2-oxo-2*H*-1-benzopyran-3-yl)benzoate,6) 7-(diethylamino)-3-phenylcoumarin,7) methyl 4-(7-diethylamino-2-oxo-2*H*-1-benzopyran-3-yl)benzoate,7) 7-(diethylamino)-3-(oxazol-5-yl)coumarin,8) and 7-(dimethylamino)-3-(2-oxazoly)coumarin9) have been reported. While, we reported the synthesis

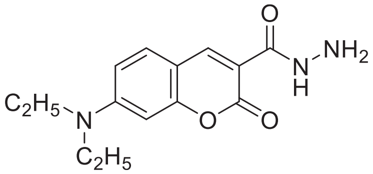

Fig. 1. Chemical structure of 7-diethylaminocoumarin-3-carboxylic acid hydrazide (**1**).

and property of 7-diethylaminocoumarin-3-carboxylic acid hydrazide (**1**, Fig. 1) as an organic fluorophore.[2)] However, the crystal structure of 7-diethylaminocoumarin-3-carboxylic acid hydrazide at 290 K has been reported by Zhang and Yin.[10)] We now report on the crystal structure of **1** at 123 K 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 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.

2.2. Material

7-diethylaminocoumarin-3-carboxylic acid hydrazide was prepared from ethyl 7-diethylaminocoumarin-3-carboxylate and hydrazine as reported by the previous paper.[2)] **1**: yellow crystals, ^1H NMR (400 MHz, $CDCl_3$) δ=1.24 (6H, *t*, *J*=6.8 Hz), 1.81 (1H, *brs*), 3.46 (4H, *q*, *J*=6.8 Hz), 4.13 (2H, *brs*), 6.49 (1H, *d*, *J*=2.4 Hz), 6.65 (1H, *dd*, *J*=8.8, 2.4 Hz), 7.43 (1H, *d*, *J*=8.8 Hz), 8.67 (1H, s), and 9.71 (1H, *s*). ^{13}C NMR (100 MHz, $CDCl_3$) δ=12.39 (2C), 45.07 (2C), 96.07, 96.59, 108.22, 109.13, 109.96, 131.10, 147.98, 152.64, 157.60, 162.04, and 162.83.

2.3. Data Collection

A yellow prism crystal of $C_{14}H_{17}N_3O_3$ having approximate dimensions of 0.500×0.300×0.100 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 triclinic cell with dimensions: a=9.2098(19) Å, b=12.619(3) Å, c=12.940(3) Å, α=94.734(15)°, β=109.987(14)°, γ=105.328(14)°, and V=1338.0(5) Å^3. For Z=4 and *F.W.*=275.31, the calculated density is 1.367 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: $P\bar{1}$ (#2). The data were collected at a temperature of -150 ± 1℃ to a maximum 2θ value of 136.5°. A total of 70 oscillation images were collected. A sweep of data was done using ω scans from 50.0 to 260.0° in 15.0° step, at $\chi=50.0^\circ$ and $\varphi=0.0^\circ$. The exposure rate was 30.0 [sec./°]. A second sweep was performed using ω scans from 50.0 to 260.0° in 15.0° step, at $\chi=50.0^\circ$ and $\varphi=90.0^\circ$. The exposure rate was 30.0 [sec./°]. Another sweep was performed using ω scans from 50.0 to 260.0° in 15.0° step, at $\chi=50.0^\circ$ and $\varphi=270.0^\circ$. The exposure rate was 30.0 [sec./°]. Another sweep was performed using ω scans from 50.0 to 260.0° in 15.0° step, at $\chi=50.0^\circ$ and $\varphi=270.0^\circ$. The exposure rate was 30.0 [sec./°]. Another sweep was performed using ω scans from 50.0 to 260.0° in 15.0° step, at $\chi=0.0^\circ$ and $\varphi=0.0^\circ$. The exposure rate was 30.0 [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 17099 reflections that were collected, 4709 were unique ($R_{int}=0.026$); equivalent reflections were merged. The linear absorption coefficient, μ, for Cu-Kα radiation is 8.089 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.646 to 0.922. 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. 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 4709 observed reflections and 386 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of: $R_1=\Sigma\|F_0|-|F_c\|/\Sigma|F_0|=0.0449$, $wR_2=[\Sigma(w(F_0^2-F_c^2)^2)/\Sigma w(F_0^2)^2]^{1/2}=0.1234$. 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, N_v= number of variables) was 1.12. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.37 and -0.35 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 $\Delta f'$ and $\Delta f''$ 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 *CrystalStructure4. 0*[16] crystallographic software package except for refinement, which was performed using *SHELXL97*[17] Fractional atomic coordinates and

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

atom	x	y	z	B_{eq}
O1	0.78287(13)	−0.04752(9)	0.40352(9)	1.86(2)
O2	0.73054(14)	−0.17682(9)	0.25962(10)	2.26(2)
O3	0.92108(15)	0.06917(9)	0.09676(10)	2.41(2)
O4	0.76662(13)	0.45165(9)	0.43223(9)	2.02(2)
O5	0.85431(14)	0.43863(10)	0.29501(10)	2.43(2)
O6	0.51465(15)	0.11527(10)	0.15204(10)	2.68(2)
N1	0.80670(18)	−0.11585(12)	0.08430(12)	2.16(2)
N2	0.8017(2)	−0.14912(12)	−0.02415(13)	2.44(2)
N3	0.87066(17)	0.20966(11)	0.72564(11)	2.07(2)
N4	0.69889(19)	0.25567(13)	0.12450(12)	2.40(2)
N5	0.6802(2)	0.19881(14)	0.01935(13)	2.71(2)
N6	0.59998(17)	0.51165(11)	0.73717(11)	2.03(2)
C1	0.78950(18)	−0.07739(13)	0.30057(13)	1.78(2)
C2	0.86355(18)	0.01165(13)	0.25287(13)	1.75(2)
C3	0.92998(19)	0.11870(13)	0.31275(13)	1.83(2)
C4	0.92498(18)	0.14695(13)	0.41859(13)	1.79(2)
C5	0.98633(19)	0.25596(13)	0.48444(13)	1.96(2)
C6	0.9685(2)	0.27729(13)	0.58361(14)	2.02(2)
C7	0.88704(19)	0.18903(13)	0.62647(13)	1.91(2)
C8	0.82544(19)	0.07939(13)	0.56146(13)	1.84(2)
C9	0.84591(18)	0.06138(13)	0.46203(13)	1.73(2)
C10	0.86611(19)	−0.00937(13)	0.13826(13)	1.88(2)
C11	0.9188(2)	0.32433(14)	0.78713(14)	2.25(3)
C12	1.0981(2)	0.36717(14)	0.86343(14)	2.55(3)
C13	0.7903(2)	0.12064(14)	0.77230(14)	2.15(2)
C14	0.6066(2)	0.09417(15)	0.72520(16)	2.56(3)
C15	0.7584(2)	0.39200(14)	0.33532(13)	1.95(2)
C16	0.63714(19)	0.28177(13)	0.29090(13)	1.93(2)
C17	0.5415(2)	0.24123(13)	0.34833(14)	2.03(2)
C18	0.5517(2)	0.30369(13)	0.44767(13)	1.94(2)
C19	0.4542(2)	0.26867(13)	0.50983(14)	2.11(2)
C20	0.4695(2)	0.33473(14)	0.60400(14)	2.04(2)
C21	0.58689(19)	0.44402(13)	0.64431(13)	1.84(2)
C22	0.68699(19)	0.47957(13)	0.58377(13)	1.94(2)
C23	0.66715(19)	0.41093(13)	0.48871(13)	1.82(2)
C24	0.6134(2)	0.21057(14)	0.18425(13)	2.01(2)
C25	0.4965(2)	0.47489(14)	0.80036(14)	2.24(3)
C26	0.5588(2)	0.40532(15)	0.88577(14)	2.62(3)
C27	0.7296(2)	0.61968(14)	0.78449(14)	2.29(3)
C28	0.8982(2)	0.61163(15)	0.84631(15)	2.59(3)

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

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 CCDC1833740 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

Table 2. Anisotropic displacement parameters (Å^2)

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0257(5)	0.0187(5)	0.0265(5)	0.0039(4)	0.0129(4)	0.0028(4)
O2	0.0332(6)	0.0199(5)	0.0333(6)	0.0032(4)	0.0178(5)	0.0016(4)
O3	0.0399(6)	0.0256(6)	0.0327(6)	0.0096(5)	0.0215(5)	0.0081(4)
O4	0.0283(6)	0.0233(5)	0.0279(5)	0.0047(4)	0.0161(5)	0.0058(4)
O5	0.0335(6)	0.0292(6)	0.0338(6)	0.0051(5)	0.0210(5)	0.0070(5)
O6	0.0396(7)	0.0286(6)	0.0314(6)	0.0052(5)	0.0157(5)	0.0026(5)
N1	0.0345(7)	0.0239(7)	0.0260(7)	0.0074(6)	0.0159(6)	0.0035(5)
N2	0.0375(8)	0.0297(7)	0.0287(7)	0.0089(6)	0.0184(6)	0.0020(6)
N3	0.0268(7)	0.0237(6)	0.0268(7)	0.0038(5)	0.0124(5)	0.0014(5)
N4	0.0344(8)	0.0320(8)	0.0274(7)	0.0086(6)	0.0163(6)	0.0041(6)
N5	0.0417(9)	0.0408(9)	0.0264(7)	0.0176(8)	0.0166(7)	0.0055(6)
N6	0.0275(7)	0.0250(7)	0.0272(7)	0.0065(5)	0.0147(5)	0.0052(5)
C1	0.0196(7)	0.0233(8)	0.0260(8)	0.0072(6)	0.0098(6)	0.0042(6)
C2	0.0197(7)	0.0227(7)	0.0264(8)	0.0077(6)	0.0100(6)	0.0063(6)
C3	0.0205(7)	0.0226(7)	0.0279(8)	0.0063(6)	0.0101(6)	0.0089(6)
C4	0.0199(7)	0.0214(7)	0.0256(8)	0.0056(6)	0.0078(6)	0.0054(6)
C5	0.0232(7)	0.0211(7)	0.0274(8)	0.0034(6)	0.0084(6)	0.0070(6)
C6	0.0246(8)	0.0200(7)	0.0272(8)	0.0039(6)	0.0069(6)	0.0017(6)
C7	0.0197(7)	0.0264(8)	0.0248(8)	0.0073(6)	0.0066(6)	0.0044(6)
C8	0.0216(7)	0.0224(7)	0.0263(8)	0.0045(6)	0.0113(6)	0.0058(6)
C9	0.0179(7)	0.0191(7)	0.0260(8)	0.0050(6)	0.0061(6)	0.0029(6)
C10	0.0215(7)	0.0242(7)	0.0286(8)	0.0092(6)	0.0109(6)	0.0071(6)
C11	0.0327(9)	0.0257(8)	0.0279(8)	0.0080(7)	0.0141(7)	0.0011(6)
C12	0.0374(10)	0.0276(8)	0.0253(8)	0.0045(7)	0.0091(7)	0.0020(6)
C13	0.0325(9)	0.0257(8)	0.0268(8)	0.0087(7)	0.0153(7)	0.0056(6)
C14	0.0322(9)	0.0288(8)	0.0428(10)	0.0089(7)	0.0217(8)	0.0106(7)
C15	0.0269(8)	0.0259(8)	0.0258(8)	0.0102(6)	0.0130(7)	0.0089(6)
C16	0.0262(8)	0.0247(8)	0.0260(8)	0.0103(6)	0.0115(6)	0.0083(6)
C17	0.0277(8)	0.0210(7)	0.0282(8)	0.0063(6)	0.0109(7)	0.0058(6)
C18	0.0257(8)	0.0225(7)	0.0262(8)	0.0060(6)	0.0111(6)	0.0076(6)
C19	0.0278(8)	0.0226(7)	0.0283(8)	0.0027(6)	0.0121(7)	0.0069(6)
C20	0.0250(8)	0.0274(8)	0.0270(8)	0.0048(6)	0.0137(6)	0.0097(6)
C21	0.0255(8)	0.0237(7)	0.0241(7)	0.0099(6)	0.0111(6)	0.0083(6)
C22	0.0259(8)	0.0213(7)	0.0269(8)	0.0052(6)	0.0115(6)	0.0072(6)
C23	0.0243(8)	0.0237(8)	0.0262(8)	0.0085(6)	0.0133(6)	0.0113(6)
C24	0.0260(8)	0.0259(8)	0.0265(8)	0.0108(6)	0.0096(6)	0.0080(6)
C25	0.0326(9)	0.0287(8)	0.0298(8)	0.0099(7)	0.0187(7)	0.0055(6)
C26	0.0338(9)	0.0331(9)	0.0266(8)	0.0015(7)	0.0106(7)	0.0066(7)
C27	0.0336(9)	0.0230(8)	0.0324(8)	0.0071(7)	0.0169(7)	0.0015(6)
C28	0.0304(9)	0.0340(9)	0.0328(9)	0.0053(7)	0.0158(7)	−0.0009(7)

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

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3. Result & Discussion

7-Diethylaminocoumarin-3-carboxylic acid hydrazide (**1**) was prepared from ethyl 7-diethylaminocoumarin-3-carboxylate and hydrazine as reported by the previous paper.2) Single crystals of **1** were obtained from the mixtures of ethyl acetate and chloroform (1:1 *v/v*). The lattice constants of **1** at 123 K and 290 K were listed in Table 3. All lattice constants at 123 K are smaller than those at 290 K.

The H atoms of the NH and $\mathrm{NH_2}$ groups were locaed in a difference map and its position and U_{iso} value were freely refined. All C-bound H atoms were positioned with the idealized geometry and were refined to be isotropic ($U_{\mathrm{iso}}(\mathrm{H})=1.2U_{\mathrm{eq}}$ (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.

Table 3. Lattice constants of **1** at 123 K and 290 K10)

Lattice constants	**1** at 123 K	**1** at 290 K10)
a (Å)	9.2098(19)	9.3438(19)
b (Å)	12.619(3)	12.771(3)
c (Å)	12.940(3)	12.978(3)
α (°)	94.734(15)	95.17(3)
β (°)	109.987(14)	110.13(3)
γ (°)	105.328(14)	106.18(3)
V (Å^3)	1338.0(5)	1366.4(5)

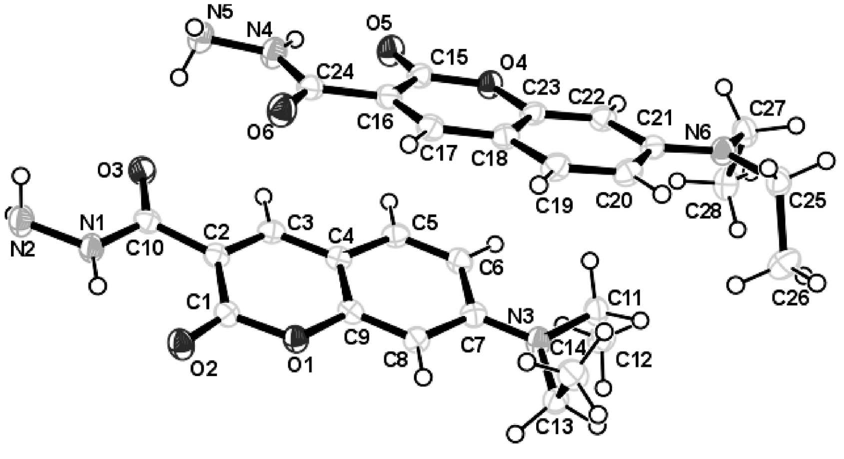

Fig. 2. An ORTEP drawing of **1** showing 50% probability displacement ellipsoids.

The structure of **1** contains two crystallographically independent molecules (**1a** and **1b**) with different conformations of the diethylamino groups. The two diethyl groups of diethylamine group of **1a** are *anti* with respect to one another. While the two diethyl groups of diethylamine group of **1b** are *syn* with respect to one another. The C—C and C—O bond lengths of coumarin ring system agree with those coumarin, as shown in Table 4.

Table 4. Selected geometric parameters (Å,°)

O1-C1	1.380(2)	O1-C9	1.3801(18)
O2-C1	1.2179(17)	O3-C10	1.239(2)
O4-C15	1.376(2)	O4-C23	1.381(2)
O5-C15	1.221(2)	O6-C24	1.2357(18)
N1-N2	1.413(2)	N1-C10	1.337(2)
N3-C7	1.355(2)	N3-C11	1.467(2)
N3-C13	1.467(2)	N4-N5	1.418(2)
N4-C24	1.339(2)	N6-C21	1.365(2)
N6-C25	1.468(2)	N6-C27	1.4698(18)
C1-C2	1.451(2)	C2-C3	1.366(2)
C2-C10	1.494(2)	C3-C4	1.406(2)
C4-C5	1.416(2)	C4-C9	1.406(2)
C5-C6	1.363(2)	C6-C7	1.434(2)
C7-C8	1.418(2)	C8-C9	1.372(2)
C11-C12	1.522(2)	C13-C14	1.519(2)
C15-C16	1.4561(19)	C16-C17	1.364(2)
C16-C24	1.498(2)	C17-C18	1.412(2)
C18-C19	1.411(2)	C18-C23	1.4066(19)
C19-C20	1.361(2)	C20-C21	1.432(2)
C21-C22	1.413(2)	C22-C23	1.372(2)
C25-C26	1.521(2)	C27-C28	1.520(2)
N1-H1	0.88(2)	N4-H18	0.859(19)
N2-H2	0.94(2)	N5-H19	0.89(2)
N2-H3	0.93(2)	N5-H20	0.91(2)
C1-O1-C9	122.81(13)	C15-O4-C23	122.96(11)
N2-N1-C10	123.36(15)	C7-N3-C11	121.34(14)
C7-N3-C13	122.30(13)	C11-N3-C13	116.10(15)
N5-N4-C24	122.59(13)	C21-N6-C25	121.53(12)
C21-N6-C27	121.10(15)	C25-N6-C27	117.09(13)
O1-C1-O2	115.40(15)	O1-C1-C2	117.28(12)
O2-C1-C2	127.32(16)	C1-C2-C3	119.53(16)
C1-C2-C10	122.00(13)	C3-C2-C10	118.45(15)
C2-C3-C4	122.22(15)	C3-C4-C5	125.77(15)
C3-C4-C9	118.04(13)	C5-C4-C9	116.12(16)
C4-C5-C6	122.12(15)	C5-C6-C7	120.99(14)
N3-C7-C6	121.19(13)	N3-C7-C8	121.38(15)
C6-C7-C8	117.43(16)	C7-C8-C9	119.79(15)

O1-C9-C4	120.00(15)	O1-C9-C8	116.46(14)
C4-C9-C8	123.53(14)	O3-C10-N1	122.60(16)
O3-C10-C2	120.70(13)	N1-C10-C2	116.70(15)
N3-C11-C12	112.46(16)	N3-C13-C14	112.34(14)
O4-C15-O5	115.59(12)	O4-C15-C16	117.63(16)
O5-C15-C16	126.78(16)	C15-C16-C17	119.05(15)
C15-C16-C24	122.46(16)	C17-C16-C24	118.50(12)
C16-C17-C18	122.49(13)	C17-C18-C19	125.71(13)
C17-C18-C23	117.96(17)	C19-C18-C23	116.32(15)
C18-C19-C20	122.21(13)	C19-C20-C21	120.81(17)
N6-C21-C20	121.01(17)	N6-C21-C22	121.39(12)
C20-C21-C22	117.59(15)	C21-C22-C23	119.92(13)
O4-C23-C18	119.87(15)	O4-C23-C22	117.00(12)
C18-C23-C22	123.14(17)	O6-C24-N4	121.98(16)
O6-C24-C16	120.54(17)	N4-C24-C16	117.44(13)
N6-C25-C26	114.17(16)	N6-C27-C28	114.92(15)
N2-N1-H1	117.9(14)	C10-N1-H1	118.7(14)
N1-N2-H2	106.3(16)	N1-N2-H3	108.1(12)
H2-N2-H3	109(2)	N5-N4-H18	118.3(17)
C24-N4-H18	119.1(17)	N4-N5-H19	105.5(13)
N4-N5-H20	103.1(18)	H19-N5-H20	111(2)
C1-O1-C9-C4	−1.8(2)	C1-O1-C9-C8	177.72(14)
C9-O1-C1-O2	179.16(14)	C9-O1-C1-C2	−1.3(2)
C15-O4-C23-C18	0.4(2)	C15-O4-C23-C22	−179.36(15)
C23-O4-C15-O5	−179.79(15)	C23-O4-C15-C16	0.8(2)
N2-N1-C10-O3	0.4(2)	N2-N1-C10-C2	−179.60(15)
C7-N3-C11-C12	−86.66(19)	C11-N3-C7-C6	7.0(2)
C11-N3-C7-C8	−173.47(15)	C7-N3-C13-C14	−83.9(2)
C13-N3-C7-C6	−178.98(15)	C13-N3-C7-C8	0.6(2)
C11-N3-C13-C14	90.40(17)	C13-N3-C11-C12	98.94(18)
N5-N4-C24-O6	1.3(2)	N5-N4-C24-C16	−176.48(16)
C21-N6-C25-C26	83.95(17)	C25-N6-C21-C20	0.9(2)
C25-N6-C21-C22	−179.87(15)	C21-N6-C27-C28	−73.6(2)
C27-N6-C21-C20	174.57(15)	C27-N6-C21-C22	−6.2(2)
C25-N6-C27-C28	100.3(2)	C27-N6-C25-C26	−89.97(17)
O1-C1-C2-C3	3.2(2)	O1-C1-C2-C10	−175.22(14)
O2-C1-C2-C3	−177.33(16)	O2-C1-C2-C10	4.2(2)
C1-C2-C3-C4	−2.0(2)	C1-C2-C10-O3	175.50(16)
C1-C2-C10-N1	−4.5(2)	C3-C2-C10-O3	−3.0(2)
C3-C2-C10-N1	177.04(16)	C10-C2-C3-C4	176.49(15)
C2-C3-C4-C5	−177.99(16)	C2-C3-C4-C9	−1.1(2)
C3-C4-C5-C6	176.19(17)	C3-C4-C9-O1	3.1(2)
C3-C4-C9-C8	−176.44(16)	C5-C4-C9-O1	−179.77(14)
C5-C4-C9-C8	0.7(2)	C9-C4-C5-C6	−0.7(2)
C4-C5-C6-C7	0.6(2)	C5-C6-C7-N3	179.23(16)
C5-C6-C7-C8	−0.3(2)	N3-C7-C8-C9	−179.24(15)
C6-C7-C8-C9	0.3(2)	C7-C8-C9-O1	179.92(14)

C7-C8-C9-C4	−0.6(2)	O4-C15-C16-C17	−2.1(2)
O4-C15-C16-C24	178.14(15)	O5-C15-C16-C17	178.61(18)
O5-C15-C16-C24	−1.2(2)	C15-C16-C17-C18	2.2(2)
C15-C16-C24-O6	176.50(16)	C15-C16-C24-N4	−5.6(2)
C17-C16-C24-O6	−3.3(2)	C17-C16-C24-N4	174.56(16)
C24-C16-C17-C18	−178.00(16)	C16-C17-C18-C19	178.18(17)
C16-C17-C18-C23	−1.0(2)	C17-C18-C19-C20	−178.82(17)
C17-C18-C23-O4	−0.3(2)	C17-C18-C23-C22	179.39(16)
C19-C18-C23-O4	−179.58(15)	C19-C18-C23-C22	0.1(2)
C23-C18-C19-C20	0.4(2)	C18-C19-C20-C21	0.0(2)
C19-C20-C21-N6	178.37(16)	C19-C20-C21-C22	−0.9(2)
N6-C21-C22-C23	−177.90(16)	C20-C21-C22-C23	1.4(2)
C21-C22-C23-O4	178.70(14)	C21-C22-C23-C18	−1.0(2)

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-2*H*-1-benzopyran-3-yl)benzoate,[5] cholesteryl 4-(7-diethylamino-2-oxo-2*H*-1-benzopyran-3-yl) benzoate,[6] 7-(diethylamino)-3-phenylcoumarin,[7] methyl 4-(7-diethylamino-2-oxo-2*H*-1-benzopyran-3-yl)benzoate,[7] 7-(diethylamino)-3-(oxazol-5-yl)coumarin,[8] and 7-(dimethylamino)-3-(2-oxazoly) coumarin[9]. The N3-C7 and N6-C21bond lengths are close to that of the value (1.355 Å)[18] 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, C11, C13 and N3 are −0.013(1) Å, −0.013(1) Å, −0.013(1) Å, and 0.029(1) Å, respectively. While, those of each atom from the least-squares plane defined by atoms C21, C25, C27 and N6 are 0.014(1) Å, 0.014(1) Å, 0.014(1) Å, and 0.031(1) Å, respectively.

The coumarin-3-carboxylic acid hydrazides are almost planar with a maximum deviation of 0.096(2) Å for C7 in **1a** and 0.200(2) Å for N5 in **1b**. The dihedral angles between the coumarin ring and carboxylic acid hydrazide are 5.9(1)° for **1a** and 6.8(1)° for **1b**, respectively. The angle between the planes of two molecules (**1a** and **1b**) is 15.91(2)°.

There are some intermolecular N—H···O hydrogen bonds of carboxylic acid hydrazide (Fig. 3, 4, and Table 5). The N—H···O distances are close to the intermolecular N—H···O distance [H···O: 2.00(4) Å, N···O: 2.877(4) Å, N—H···O Å: 172°] of 2-amino-5-hexyloxytropone.[19] The NH_2 group of carboxylic acid hydrazide participates in the N—H···O intermolecular hydrogen bond. Some C—H···O hydrogen bonds are shown in 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).[4–9,20] There are some intermolecular C—H···N hydrogen bonds in the crystal structure of **1b** (Fig. 5 and Table 5). The H···N distances are similar

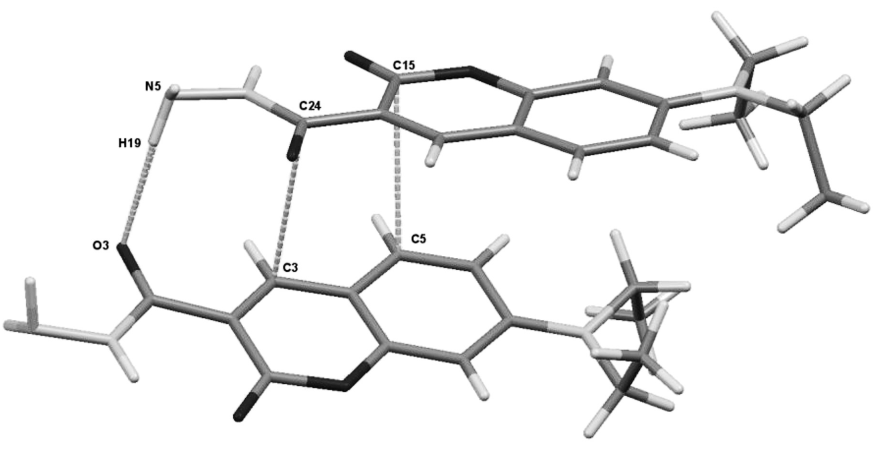

Fig. 3. Intermolecular N—H···O and $\pi\cdots\pi$ interactions in **1a** and **1b**.

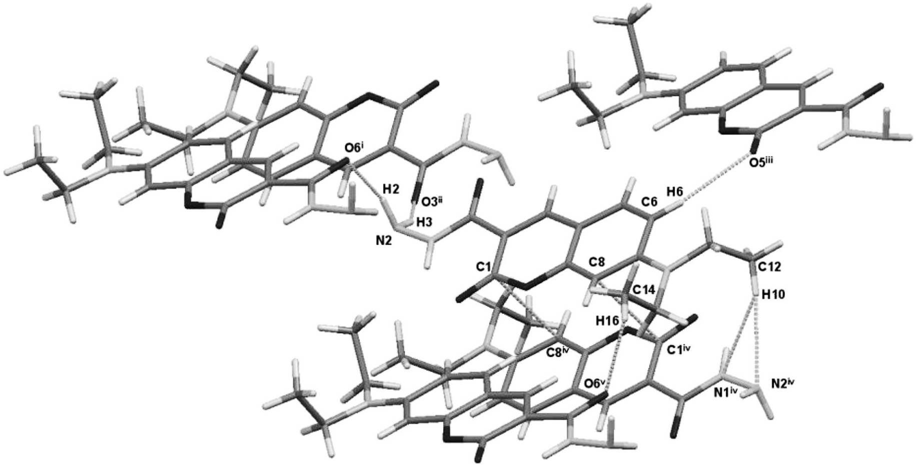

Fig. 4. Intermolecular N—H···O, C—H···O, and $\pi\cdots\pi$ interactions in **1a**.

to that (2.704 Å) of 7-(diethylamino)-3-(2-oxyazoyl)coumarin.[9)]

The Intermolecular $\pi\cdots\pi$ interactions between the coumarin planes are shown in Fig. 3 and Fig. 4. The distances between the intermolecular coumarin planes are 3.280(2) Å for C5···C15 (Fig. 3) and 3.390(2) Å (Fig. 4) for C1···C8^{v}, respectively (symmetry code: (v) 1-x, -y, 1-z). The distances are within the range associated with $\pi\cdots\pi$ interactions (3.3-3.8 Å).[5,7,21)]

In conclusion, the crystal structure of 7-diethylaminocoumarin-3-carboxylic acid hydrazide (**1**) was elucidated by X-ray crystallographic analysis. Intermolecular N—H···O, C—H···O, C—H···N, and $\pi\cdots\pi$ interactions help stabilized the crystal packing.

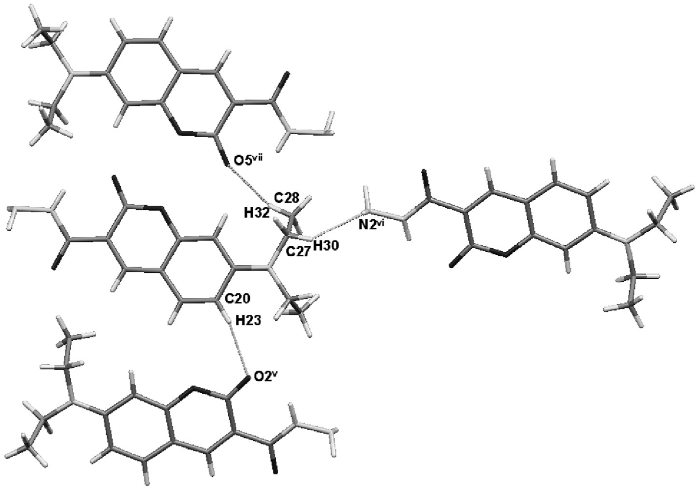

Fig. 5. Intermolecular C—H···O and C—H···N interactions in **1b**.

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
N2	H2	O6^{i}	0.94(2)	2.107	2.981(2)	154	(i) 1-x, -y, -z
N2	H3	O3^{ii}	0.93(2)	2.098	2.976(3)	133	(ii) 2-x, -y, -z
N5	H19	O3	0.89(2)	2.169	3.045(2)	167	
C6	H6	O5^{iii}	0.950	2.358	3.494(2)	168	(iii) 2-x, 1-y, 1-z
C12	H10	N1^{iv}	0.980	2.744	3.564(3)	142	(iv) 2-x, -y, 1-z
C12	H10	N2^{iv}	0.980	2.732	3.704(3)	172	(iv) 2-x, -y, 1-z
C14	H16	O6^{v}	0.980	2.423	3.332(3)	154	(v) 1-x, -y, 1-z
C20	H23	O2^{v}	0.950	2.472	3.368(2)	157	(v) 1-x, -y, 1-z
C27	H30	N2^{vi}	0.990	2.577	3.427(3)	144	(vi) x, 1+y, 1+z
C28	H32	O5^{vii}	0.980	2.581	3.516(3)	160	(vii) 2-x, 1-y, 1-z

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