Materials containing a coumarin (2H-1-benzopyran-2-one) component have been useful in many fields, such as fluorescence materials and laser dyes, nonlinear optical materials and reagents, photorefractive materials, photoresists, intermediates for drug synthesis, luminescence materials, and analytical reagents. 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 fluoroionophores accessible for analytical purposes in the fields of analytical and biological chemistry. The crystal structures of 7-(diethylamino)coumarin derivatives as fluoroionophores are necessary for the understanding of the substituent effect on the fluorescence intensity. This paper reports on the crystal structure of 7-(diethylamino)-3-(oxazol-5-yl)coumarin, which was determined in order to elucidate the substituent effect at 3- and 7-positions of coumarin on the structure and crystal packing.

Compound (I) was synthesized by the reaction of 7-(diethylamino)coumarin-3-carbaldehyde and [(4-methylphenyl)sulfonyl]methaneisocyanide in the presence of K2CO3, as reported in a previous paper. Single crystals of 1 were grown in a mixture of chloroform-methanol (1:1 v/v) at room temperature. The data collection and refinement parameters are listed in Table 1. The H atoms were positioned with the idealized geometry, and were refined to be isotropic (Uiso(H) = 1.2 Ueq(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 were observed in the crystal lattice.

The structure of 7-(diethylamino)-3-(oxazol-5-yl)coumarin was determined by X-ray crystallography. The coumarin ring makes an angle with the oxazole ring. The N atom of the diethylamine group has a planar environment. The two ethyl groups of diethylamine are anti with respect to one another. Intermolecular C–H···O, C–H···N, and C–H···p interactions were observed in the crystal lattice.
and torsion angles are collected in Table 2.

An ORTEP drawing of molecule of 1 is shown in Fig. 2. Compound (1) is almost planar. The dihedral angle between the coumarin plane (defined by C1/C2/C3/C4/C5/C6/C7/C8/C9/O1/O2) and the oxazole plane (defined by C14/C15/C16/O3/N2) is 4.54(4)˚.

The C–C and C–O bond lengths of the coumarin ring of 1 are similar to those of 7-diethylaminocoumarin, and distinct from those of coumarin, itself. The C7–N1 bond length of 1 is close to that of 7-(diethylamino)coumarin.2 A value of 1.355 Å7 is observed for a Csp²–Nsp² bond. The respective deviations of each atom from the least-squares plane defined by C6, C8, C10, and C12 are –0.050(1), 0.050(1), –0.056(1), and 0.049(1)Å. This means that the diethylamino group substituted at the C7 position effects on the conjugation system of coumarin. The two ethyl groups of the diethylamino group are anti with respect to one another.

Intermolecular C–H–O and C–H–N hydrogen bonds are observed in the crystal structure of 1 (Table 3 and Fig. 3). The H–O distances are similar to those (2.419, 2.426, and 2.495 Å)8 of 7-(diethylamino)-3-((4-ethoxycarbonyl)-thiazol-2-yl)coumarin. The H–N distance is shorter than those (2.91 and 2.739 Å) of 2,2’-bi-2-imidazoline8 and 7-(diethylamino)-3-phenylcoumarin.7 There is an intermolecular C–H–π interaction observed in the crystal structure of 1 (Table 3 and Fig. 3), with distance for this type of interaction (2.8 – 3.1 Å).14

These intermolecular C–H–O, C–H–N, and CH–π interactions help to stabilize the crystal packing.

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References