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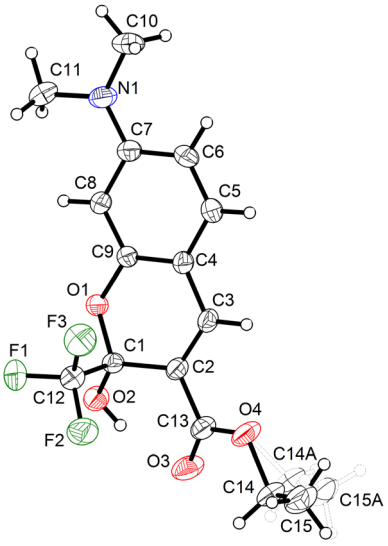
# Crystal structure of 7-(dimethylamino)-2-hydroxy-2-(trifluoromethyl)-2*H*-chromene-3-ethyl carboxylate, $C_{15}H_{16}F_3NO_4$

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**Abstract**

$C_{15}H_{16}F_3NO_4$, triclinic, $P\bar{1}$ (no. 2), $a$ = 6.7000(2) Å, $b$ = 11.7844(4) Å, $c$ = 19.3039(6) Å, $\alpha$ = 83.581(3)°, $\beta$ = 86.015(3)°; $\gamma$ = 87.713(3)°; $V$ = 1510.14 Å$^3$, $Z$ = 4, $R_{gt}(F)$ = 0.0459, w$R_{ref}(F^2)$ = 0.1389, T = 294.95 K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Green block |
| Size: | 0.30 × 0.28 × 0.18 mm |
| Wavelength: | Cu *Kα* radiation (1.54184 Å) |
| $\mu$: | 1.12 mm$^{-1}$ |
| Diffractometer, scan mode: | SuperNova, $\omega$ |
| $\theta_{max}$, completeness: | 71.5°, >99 % |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 12143, 5735, 0.020 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\sigma(I_{obs})$, 4,731 |
| $N(param)_{refined}$: | 443 |
| Programs: | CrysAlis$^{PRO}$,[1] Olex2,[2] Shelx[3,4] |

## 1 Source of material

The title compound, 7-(dimethylamino)-2-hydroxy-2-(trifluoromethyl)-2*H*-chromene-3-ethyl carboxylate was synthesized according to the literature method with slight modification.[5] Anhydrous ethanol was selected as the reaction solvent for the condensation between 4-dimethylaminosalicylaldehyde and ethyl trifluoroacetoacetate, by which the synthetic yield can be increased more higher than reagent grade ethanol. In a 100 mL round bottom flask, 4-dimethylaminosalicylaldehyde (826 mg, 5 mmol) and ethyl trifluoroacetoacetate (1.013 g, 5.5 mmol) was dissolved in 60 mL anhydrous ethanol. Piperidine (0.04 mmol) was added and the mixture was heated to reflux for about 5 h. The reaction progress was monitored with thin layer chromatography (TLC). When the starting 4-dimethylaminosalicylaldehyde disappeared completely on the TLC plate, the reaction was quenched by adding distilled water 40 mL. The reaction mixture was extracted with dichloromethane (50 mL × 3). The organic part was combined and washed with distilled water (500 mL × 3). The collected organic phase was dried over $MgSO_4$. The volatile components were evaporated on the rotary evaporating equipment. The residue was purified by column chromatography on silica gel (hexane/dichloromethane, 1:2). The purified 7-(dimethylamino)-2-hydroxy-2-(trifluoromethyl)-2*H*-chromene-3-ethyl carboxylate was saturated in ethanol and the suitable crystal was obtained by slow evaporation of the ethanol in a 10 mL vial with parafilm covered.

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$).

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| F1 | −0.25204 (18) | 0.76590 (11) | 0.10761 (7) | 0.0810 (4) |
| F2 | −0.0468 (2) | 0.88036 (10) | 0.04791 (7) | 0.0849 (4) |
| F3 | 0.0509 (2) | 0.77173 (12) | 0.13674 (6) | 0.0830 (4) |
| O1 | −0.02201 (15) | 0.57825 (10) | 0.07778 (6) | 0.0512 (3) |
| O2 | −0.13767 (18) | 0.68448 (12) | −0.01389 (6) | 0.0592 (3) |
| H2 | −0.0919 | 0.7151 | −0.0516 | 0.089* |
| O3 | 0.1256 (2) | 0.80847 (15) | −0.10034 (7) | 0.0799 (5) |
| O4 | 0.4233 (2) | 0.83167 (13) | −0.06084 (7) | 0.0717 (4) |
| N1 | 0.1920 (3) | 0.29191 (13) | 0.25195 (8) | 0.0604 (4) |
| C1 | 0.0030 (2) | 0.68309 (13) | 0.03483 (8) | 0.0437 (3) |
| C2 | 0.2160 (2) | 0.70113 (14) | 0.00482 (8) | 0.0457 (4) |
| C3 | 0.3675 (2) | 0.63964 (14) | 0.03413 (8) | 0.0472 (4) |
| H3 | 0.4984 | 0.6545 | 0.0173 | 0.057* |
| C4 | 0.3323 (2) | 0.55181 (14) | 0.09069 (8) | 0.0449 (3) |
| C5 | 0.4824 (2) | 0.48718 (16) | 0.12521 (10) | 0.0552 (4) |
| H5 | 0.6156 | 0.5023 | 0.1119 | 0.066* |
| C6 | 0.4394 (3) | 0.40230 (16) | 0.17803 (10) | 0.0566 (4) |
| H6 | 0.5433 | 0.3618 | 0.2002 | 0.068* |
| C7 | 0.2386 (3) | 0.37554 (13) | 0.19920 (8) | 0.0477 (4) |
| C8 | 0.0871 (2) | 0.43842 (13) | 0.16353 (8) | 0.0449 (3) |
| H8 | −0.0464 | 0.4220 | 0.1753 | 0.054* |
| C9 | 0.1352 (2) | 0.52395 (13) | 0.11133 (8) | 0.0414 (3) |
| C10 | 0.3437 (4) | 0.23497 (18) | 0.29471 (11) | 0.0730 (6) |
| H10A | 0.4358 | 0.1925 | 0.2663 | 0.110* |
| H10B | 0.2811 | 0.1838 | 0.3312 | 0.110* |
| H10C | 0.4148 | 0.2909 | 0.3149 | 0.110* |
| C11 | −0.0154 (3) | 0.27141 (19) | 0.27426 (12) | 0.0746 (6) |
| H11A | −0.0764 | 0.3388 | 0.2914 | 0.112* |
| H11B | −0.0224 | 0.2090 | 0.3108 | 0.112* |
| H11C | −0.0851 | 0.2528 | 0.2354 | 0.112* |
| C12 | −0.0619 (3) | 0.77639 (16) | 0.08199 (10) | 0.0587 (4) |
| C13 | 0.2471 (3) | 0.78469 (16) | −0.05705 (9) | 0.0542 (4) |
| C14[a] | 0.4567 (10) | 0.9236 (5) | −0.1186 (2) | 0.0726 (13) |
| H14A[a] | 0.4915 | 0.8909 | −0.1620 | 0.087* |
| H14B[a] | 0.3356 | 0.9707 | −0.1243 | 0.087* |
| C15[a] | 0.6182 (9) | 0.9926 (6) | −0.1024 (4) | 0.0931 (17) |
| H15A[a] | 0.6660 | 1.0388 | −0.1438 | 0.140* |
| H15B[a] | 0.7255 | 0.9435 | −0.0848 | 0.140* |
| H15C[a] | 0.5700 | 1.0410 | −0.0676 | 0.140* |
| F4 | 0.61872 (19) | 0.13185 (11) | 0.42112 (6) | 0.0728 (3) |
| F5 | 0.93038 (18) | 0.13384 (12) | 0.44069 (7) | 0.0842 (4) |
| F6 | 0.7345 (2) | 0.02022 (10) | 0.50549 (7) | 0.0760 (3) |
| O5 | 0.72341 (16) | 0.32348 (10) | 0.47936 (6) | 0.0518 (3) |
| O6 | 0.85351 (17) | 0.21275 (12) | 0.56633 (7) | 0.0624 (4) |
| H6A | 0.8242 | 0.1693 | 0.6015 | 0.094* |
| O7 | 0.61327 (19) | 0.08050 (13) | 0.65234 (7) | 0.0679 (4) |
| O8 | 0.28423 (17) | 0.11278 (10) | 0.64710 (6) | 0.0525 (3) |
| N2 | 0.4889 (3) | 0.60856 (13) | 0.30756 (8) | 0.0603 (4) |
| C00L | 0.5627 (2) | 0.37775 (13) | 0.44773 (8) | 0.0417 (3) |
| C16 | 0.7007 (2) | 0.21732 (14) | 0.52123 (8) | 0.0460 (4) |
| C17 | 0.4929 (2) | 0.20471 (13) | 0.55780 (8) | 0.0418 (3) |
| C18 | 0.3383 (2) | 0.26640 (13) | 0.53052 (8) | 0.0428 (3) |
| H18 | 0.2094 | 0.2542 | 0.5504 | 0.051* |
| C19 | 0.3674 (2) | 0.35014 (13) | 0.47172 (8) | 0.0428 (3) |
| C20 | 0.2126 (2) | 0.41401 (15) | 0.43883 (9) | 0.0514 (4) |
| H20 | 0.0805 | 0.3990 | 0.4540 | 0.062* |
| C21 | 0.2504 (3) | 0.49776 (15) | 0.38509 (10) | 0.0551 (4) |
| H21 | 0.1440 | 0.5376 | 0.3641 | 0.066* |
| C22 | 0.4486 (3) | 0.52480 (13) | 0.36098 (8) | 0.0481 (4) |
| C23 | 0.6053 (2) | 0.46239 (13) | 0.39464 (8) | 0.0470 (4) |
| H23 | 0.7377 | 0.4787 | 0.3808 | 0.056* |
| C24 | 0.6923 (4) | 0.62894 (18) | 0.28064 (11) | 0.0717 (6) |
| H24A | 0.7682 | 0.6510 | 0.3170 | 0.108* |
| H24B | 0.6926 | 0.6889 | 0.2426 | 0.108* |
| H24C | 0.7512 | 0.5604 | 0.2643 | 0.108* |
| C25 | 0.3285 (4) | 0.66528 (17) | 0.26848 (11) | 0.0707 (6) |
| H25A | 0.2570 | 0.6095 | 0.2483 | 0.106* |
| H25B | 0.3841 | 0.7193 | 0.2320 | 0.106* |
| H25C | 0.2384 | 0.7045 | 0.2993 | 0.106* |
| C26 | 0.7465 (3) | 0.12477 (16) | 0.47182 (10) | 0.0573 (4) |
| C27 | 0.4733 (2) | 0.12698 (14) | 0.62234 (8) | 0.0472 (4) |
| C28 | 0.2579 (3) | 0.04071 (17) | 0.71284 (9) | 0.0603 (5) |
| H28A | 0.3353 | 0.0686 | 0.7477 | 0.072* |
| H28B | 0.3036 | −0.0370 | 0.7069 | 0.072* |
| C29 | 0.0432 (3) | 0.0434 (2) | 0.73559 (11) | 0.0741 (6) |
| H29A | −0.0317 | 0.0135 | 0.7015 | 0.111* |
| H29B | −0.0012 | 0.1207 | 0.7404 | 0.111* |
| H29C | 0.0228 | −0.0024 | 0.7797 | 0.111* |
| C14A[b] | 0.515 (2) | 0.8860 (15) | −0.1260 (6) | 0.076 (3) |
| H14C[b] | 0.5545 | 0.8256 | −0.1550 | 0.091* |
| H14D[b] | 0.4109 | 0.9319 | −0.1493 | 0.091* |
| C15A[b] | 0.6589 (19) | 0.9466 (16) | −0.1267 (8) | 0.087 (4) |
| H15D[b] | 0.6499 | 1.0082 | −0.1635 | 0.131* |
| H15E[b] | 0.7800 | 0.9021 | −0.1346 | 0.131* |
| H15F[b] | 0.6602 | 0.9770 | −0.0827 | 0.131* |

[a]Occupancy: 0.702 (18), [b]Occupancy: 0.298 (18).

## 2 Experimental details

Hydrogen atoms attached to C atoms were placed geometrically and refined using a riding model approximation, with *d*(C–H) = 0.93 Å, 0.96 Å, or 0.97 Å(–CH, $-CH_3$, $-CH_2$). $U_{iso}$(H) = 1.2 $U_{eq}$(C) for CH or $U_{iso}$(H) = 1.5 $U_{eq}$(C) for $CH_3$ and $CH_2$ groups.[3] The ethyl group attached to O4 is positionally disordered and rotates around the O4. And it was split into two parts with 70 % and 30 %, respectively. The distance of O4–C14/O4–C14A and C15–C14/C15A–C14A was restricted to be identical by SADI command. RIGU command was used to restrict thermal ellipsoids to a reasonable extent. Interestingly, the ethyl group (C28–C29) of another molecule in the asymmetrical unit is ordered.

## 3 Comment

The 7-(dimethylamino)-2-hydroxy-2-(trifluoromethyl)-2*H*-chromene-3-ethyl carboxylate is a coumarin-containing

fluorescent dye and has strong fluorescence emission in crystal state. Therefore, these coumarin based fluorescent dyes were developed in construction of fluorescent probe, bio-marker, solar cell, etc.[6–10] The crystal dye structure with a build in electron donor (dimethylamino) and electron acceptor (carbonyl and trifluoromethyl) constructed intramolecular electron push-pull system. With the specifically character of $\pi$ system of coumarin, the emission behavior can be modified according to the requirement of material and device fabrication. In this case, the fluorescence emission maximum value can be shifted to longer wavelength smoothly.[11–13] OLED can be fabricated based on the highly efficient emiting dyes.

In the title crystal structure, the asymmetric unit contains two molecules. Both the bond lengths and the angles are in the expected ranges. The coumarin part in the dye structure is coplanar with the root mean square error (RMSD) in distance estimated to be 0.07 and 0.64 Å, respectively. Due to the nucleophilic addition of trifluoromethyl to the carbonyl, the hybridized $sp^2$ C1 and C16 transformed to $sp^3$ hybridization. Therefore, C1 and C16 are slightly twisted out of the coumarin plane. The distance of C2–C13 and C17–C27 are estimated to be 1.469 and 1.463 Å, which is shorter than the general saturated carbons. However, the carbonyl group (C13–O3 and C47–O7) twist from coumarin plane and the conjugation between the two parts disconnect. Vice versa, the distance of N1–C7 and N2–C22 are determined to be 1.364 and 1.366 Å, which is shorter than N1–C10/N1–C11 and N2–C24/N2–C25 (the distance ranging from 1.444 to 1.454 Å). It indicates that N1/N2 conjugates with the corresponding coumarin system, which facilitates the electron donation from N atom to coumarin part. Totally, the donor ($NMe_2$) and the acceptor (carbonyl group), together with the coumarin moiety, jointly configured the intramolecular electron "push-pull" effect in a fluorescent dye system. Due to the electronic "push-pull" effect, one can effectively configure a modifiable fluorescent dye.[14–18] Furtherly, the structure of amino (N1/C7/C10/C11 and N2/C22/C24/C25) formed the planar rather than the trigonal pyramid geometry with the RMSD in distance 0.032 and 0.033 Å, respectively. It demonstrates the electron donation character of N1/N2. The adjacent parallel molecules are jointed by strong $\pi\cdots\pi$ interaction. The distance between the two parallel coumarin plane (C16/C17/C18/C19/C20/C21/C22/C23/C30/O5$^{i1}$ and C16/C17/C18/C19/C20/C21/C22/C23/C30/O5$^{i2}$ *i*1: $-x$, $1-y$, $1-z$; *i*2: $-1+x$, $y$, $z$.) is determined to be 3.617 Å. The coumarin plane centroid distance is 3.784 Å and the parallel shift is 1.1 Å, corresponding to the parallel-displaced geometry.[19] Typical inter-/intramolecular C–H···O interactions are established. In the adjacent non-parallel molecules, four hydrogen bonds are observed (C5–H5···O1$^{i3}$, C15A–H15E···O3$^{i3}$, C20–H20···O5$^{i4}$, C18–H18···O6$^{i4}$, *i*3: $-x$, $2-y$, $-z$; *i*4: $-1+x$, $y$, $z$.) with the C···O contacts ranging from 3.343 to 3.610 Å, C–H···O angle ranging from 162.5 to 172.6°. Also, there exists two intramolecular hydrogen bonds (O2–H2···O3$^{i5}$, O6–H6A···O7$^{i2}$, *i*5: $1-x$, $2-y$, $-z$) with the O···O contacts 2.698/2.651 Å and O–H···O 145.8/144.8°. The distances of C···O distances are well inside the interval of 3.0–4.0 Å and quoted by Desiraju.[20] And C–H···O angles are also in agreement with the above mentioned survey.[20,21] Additionally, the fluorine atom also involved in the hydrogen bond construction. The typical H···F contacts are C11–H11B···F5$^{i6}$, C24–H24B···F1$^{i6}$, and C14–H14B···F2$^{i6}$ (*i*6: $x$, $y$, $z$). The H···F distance ranges from 3.435 to 3.545 Å. The hydrogen bonds configuration in the crystal is significant to understand the behavior of the fluorescent dyes.[22–26] Therefore, introduction of heteroatoms is beneficial to establish various inter- and/or intra-molecular hydrogen bonds, with which the radiative and nonradiative channels ratio is modifiable.[27] The stronger intramolecular interactions can quench the fluorescent emission of dye effectively.[28–31]

In the crystal, the molecules were regularly packed by hydrogen bonds and $\pi\cdots\pi$ interactions. The driving force of parallel molecules packing is based on the $\pi\cdots\pi$ interaction mainly. While, the hydrogen bonds jointed the parallel molecules side by side. The weak interactions mentioned above determines its highly emissive character in solid state.[32] With no stronger T-shaped $\pi\cdots\pi$ interaction, a regular tight packing is avoided and thus ignite a highly fluorescent emission.[33–37] The nonradiative channel of excited dye molecules is inhibited to a large extent.[38,39] For 7-(dimethylamino)-2-hydroxy-2-(trifluoromethyl)-2*H*-chromene-3-ethyl carboxylate, the unique packing style, together with the intramolecular electron "push-pull" effect, leads to the unique emisson character in crystal state.[40,41] It shows that reasonable configuration of inter- and intra-molecular interaction based on heteroatoms and aromatic system is important in molecular designing.[42–44] In conclusion, the molecules are staggered layer by layer along with the axis *b* and *c*. The hydrogen bonds join the layers.

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**Author contribution:** All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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