Crystal structure of 3-carboxyethyl-7-diethylaminocoumarin, $C_{16}H_{19}NO_4$

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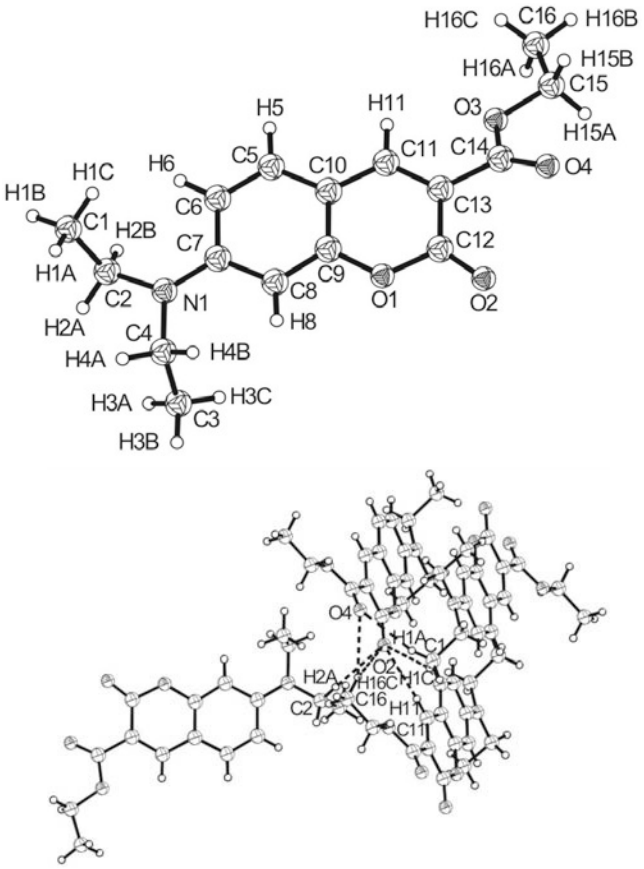

Abstract

$C_{16}H_{19}NO_4$, monoclinic, $P12_1/c1$ (no. 14), a = 6.744(1) Å, b = 15.846(3) Å, c = 13.375(3) Å, β = 97.36(3)°, V = 1417.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.067, $wR_{ref}(F^2)$ = 0.176, T = 293 K.

Source of material

3-Carboxyethyl-7-diethylaminocoumarin is commercially available. It can also be synthesized easily according to the reported methods [1-3]. Chemicals used for the synthesis were commercially available of AR grade, and were used as received without further purification. The yellow crystals of the title compound were obtained by slowly evaporating of ethanol solution at room temperature. The crystalline solid product thus was filtered, washed with ethanol and dried. Single crystals suitable for X-ray diffraction were obtained by recrystallization from ethanol.

Discussion

The interatomic distances within the molecule (figure, top) are in the normal range. Obviously $\pi\cdots\pi$ interactions were found between parallel molecules (figure, bottom). The centroid···centroid distance is 3.844(1) Å and the angle between the ring normal and the vectors of two interacted ring centroids is 29.59(1)°. The shorter atom-atom contact between the two parallel planes is 3.481(2) Å (C8^{i} to O1^{ii}, i: 1–x,0.5+y,1.5+z; ii: –1+x,1.5–y, –0.5+z), characteristic for a weak interaction [4]. However, the crystal was not packed layer by layer. The crystal generated only by one kind of hydrogen bond (C5–H5···O1^{iii}, iii: –1+x,1.5–y, –0.5+z). The donor-acceptor distance is 2.654(1) Å with the bond angle 170.0(1)°. Another interactions that can not be neglected is the weak C–H···O bond. Totally six kinds of C–H···O interactions are found: C1–H1C···O2^{iv} (iv: –1+x,1.5–y,–0.5+z), C16–H16C···O2^{iv}, C2–H2A…O2^{iv}, C11–H11···O2^{iv}, C16–H16C···O4^{iv}, and C1–H1A···O4^{iv}. The H···O distances are 2.761(2) Å (H1C···O2^{iv}), 2.753(2) Å (H16C···O2^{iv}), 2.553(2) Å (H2A···O2^{iv}), 2.521(1) Å (H11···O2^{iv}), 2.611(2) Å (H16C···O4^{iv}), and 2.672(2) Å (H16C···O4^{iv}). The C···O contacts range from 3.44 to 3.53 Å, which is well inside the interval quoted by Desiraju of 3.0 to 4.0 Å, based on a survey of over 100 structures [5]. All of the C–H···O angles range from 130.0° to 169.5°, which are also in agreement with [5]. C–H···O interactions also help to stabilize the molecular conformation of this coumarin derivative. There are several intermolecular C–H···π interactions. A typical C–H···π interaction observed is C15–H15B···π(C5-C10). The hydrogen atom is directly above the centre of the phenyl ring, which indicates that the hydrogen atom is being attracted in the direction of the ring centre. The C15···centroid(C5-C10) distance is 3.537(2) Å and the bond angle is 131.1(1)°. This geometry corresponds to a type I interactions [6]. The weak interactions including $\pi\cdots\pi$ and C–H···O interactions join the molecules into network.

Table 1. Data collection and handling.

Crystal:	yellow irregular, size 0.60 × 0.80 × 1.00 mm
Wavelength:	Synchroton, 0.90000 Å
μ:	0.97 cm^{-1}
Diffractometer, scan mode:	ADSC Quantum210, φ/ω 2° steps
$2\theta_{max}$:	60.7°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3705, 1903
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1820
$N(param)_{refined}$:	194
Programs:	SHELX-90 [7], SHELXS-97 [8], SHELXL-97 [9], DIAMOND [10]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.6490	0.2226	0.7439	0.061
H(1B)	4*e*	0.4291	0.2435	0.6976	0.061
H(1C)	4*e*	0.5189	0.2838	0.8005	0.061
H(2A)	4*e*	0.6571	0.3207	0.6151	0.041
H(2B)	4*e*	0.5165	0.3812	0.6665	0.041
H(3A)	4*e*	0.9472	0.4015	0.5596	0.060
H(3B)	4*e*	1.1743	0.3901	0.6000	0.060
H(3C)	4*e*	1.0555	0.4672	0.6355	0.060
H(4A)	4*e*	0.9865	0.2976	0.6861	0.043
H(4B)	4*e*	1.0939	0.3636	0.7620	0.043
H(5)	4*e*	0.4456	0.5487	0.9072	0.039
H(6)	4*e*	0.4814	0.4346	0.8074	0.039
H(8)	4*e*	1.0744	0.4817	0.8239	0.038
H(11)	4*e*	0.6012	0.6763	1.0036	0.038
H(15A)	4*e*	0.7443	0.9359	1.1096	0.042
H(15B)	4*e*	0.6791	0.8778	1.1952	0.042
H(16A)	4*e*	0.4228	0.9318	1.0242	0.056
H(16B)	4*e*	0.4098	0.9624	1.1346	0.056
H(16C)	4*e*	0.3562	0.8689	1.1040	0.056

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*e*	1.0894(2)	0.60909(8)	0.9345(1)	0.034(1)	0.0285(8)	0.0349(8)	–0.0008(6)	0.0048(6)	–0.0028(5)
O(2)	4*e*	1.2433(2)	0.71660(9)	1.0154(1)	0.036(1)	0.0318(8)	0.0407(8)	–0.0045(6)	0.0048(6)	–0.0038(6)
O(3)	4*e*	0.6908(2)	0.81595(8)	1.0646(1)	0.035(1)	0.0281(8)	0.0371(8)	0.0019(6)	0.0045(6)	–0.0042(5)
O(4)	4*e*	1.0082(2)	0.81339(9)	1.1406(1)	0.039(1)	0.0365(9)	0.0425(9)	0.0003(6)	–0.0002(7)	–0.0068(6)
N(1)	4*e*	0.7981(3)	0.3815(1)	0.7344(1)	0.038(1)	0.030(1)	0.0333(9)	–0.0016(7)	0.0061(7)	–0.0031(7)
C(1)	4*e*	0.5482(4)	0.2657(1)	0.7355(2)	0.048(2)	0.033(1)	0.040(1)	–0.0057(9)	0.0017(9)	–0.0005(9)
C(2)	4*e*	0.6234(3)	0.3401(1)	0.6796(1)	0.038(1)	0.032(1)	0.032(1)	0.0000(9)	0.0034(9)	–0.0032(8)
C(3)	4*e*	1.0472(3)	0.4087(1)	0.6169(2)	0.037(2)	0.045(1)	0.038(1)	–0.0004(9)	0.0076(9)	–0.0042(9)
C(4)	4*e*	0.9912(3)	0.3568(1)	0.7048(2)	0.038(1)	0.030(1)	0.038(1)	0.0027(8)	0.0033(9)	–0.0049(8)
C(5)	4*e*	0.5715(3)	0.5356(1)	0.8903(1)	0.035(1)	0.030(1)	0.032(1)	0.0005(8)	0.0057(8)	0.0028(8)
C(6)	4*e*	0.5926(3)	0.4675(1)	0.8296(1)	0.037(1)	0.029(1)	0.031(1)	–0.0023(8)	0.0034(8)	0.0020(8)
C(7)	4*e*	0.7815(3)	0.4462(1)	0.7999(1)	0.040(2)	0.026(1)	0.028(1)	0.0012(9)	0.0036(8)	0.0038(8)
C(8)	4*e*	0.9476(3)	0.4951(1)	0.8395(1)	0.035(1)	0.029(1)	0.031(1)	0.0028(8)	0.0056(8)	0.0014(8)
C(9)	4*e*	0.9222(3)	0.5627(1)	0.9012(1)	0.036(1)	0.028(1)	0.029(1)	–0.0011(8)	0.0007(8)	0.0042(8)
C(10)	4*e*	0.7357(3)	0.5861(1)	0.9277(1)	0.036(1)	0.028(1)	0.030(1)	0.0025(8)	0.0043(8)	0.0038(8)
C(11)	4*e*	0.7248(3)	0.6593(1)	0.9869(1)	0.035(1)	0.029(1)	0.030(1)	0.0021(9)	0.0051(8)	0.0032(8)
C(12)	4*e*	1.0858(3)	0.6811(1)	0.9943(1)	0.043(2)	0.024(1)	0.029(1)	0.0002(9)	0.0036(9)	0.0015(7)
C(13)	4*e*	0.8907(3)	0.7061(1)	1.0205(1)	0.037(1)	0.027(1)	0.031(1)	0.0008(8)	0.0047(8)	0.0025(8)
C(14)	4*e*	0.8761(3)	0.7831(1)	1.0821(1)	0.035(2)	0.029(1)	0.031(1)	–0.0011(9)	0.0046(9)	0.0027(8)
C(15)	4*e*	0.6555(3)	0.8905(1)	1.1238(2)	0.043(2)	0.025(1)	0.036(1)	–0.0013(8)	0.0056(9)	–0.0055(8)
C(16)	4*e*	0.4419(3)	0.9156(1)	1.0940(2)	0.043(2)	0.029(1)	0.040(1)	0.0015(9)	0.0054(9)	–0.0047(8)

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References

1. Jung, H. S.; Kwon, P. S.; Lee, J. W.; Kim, J. I.; Hong, C. S.; Kim, J. W.; Yan, S.; Lee, J. Y.; Lee, J. H.; Joo, T.; Kim, J. S.: Coumarin-Derived Cu^{2+}-Selective Fluorescence Sensor: Synthesis, Mechanisms, and Applications in Living Cells. J. Am. Chem. Soc. **131** (2009) 2008.
2. Ray, D.; Bharadwaj, P. K.: A Coumarin-Derived Fluorescence Probe Selective for Magnesium. Inorg. Chem. **47** (2008) 2252-2254.
3. Ma, Y.; Luo, W.; Quinn, P. J.; Liu, Z.; Hider, R. C.: Design, synthesis, physicochemical properties, and evaluation of novel iron chelators with fluorescent sensors. J. Med. Chem. **47** (2004) 6349-6362.
4. Janiak, C.: A critical account on π-π stacking in metal complexes with aromatic nitrogen-containing ligands. J. Chem. Soc. Dalton. Trans. **21** (2000) 3885-3896.
5. Desiraju, G. R.: The C–H···O hydrogen bond in crystals: What is it? Acc. Chem. Res. **24** (1991) 290-296.
6. Malone, J. F.; Murray, C. M.; Charlton, M. H.; Docherty, R.; Lavery, A. J.: X–H···π(phenyl) interactions theoretical and crystallographic observations. J. Chem. Soc. Faraday Trans. **93** (1997) 3429-3436.
7. Sheldrick, G. M.: Phase annealing in SHELX-90: direct methods for larger structures. Acta Crystallogr. **A46** (1990) 467-473.
8. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
9. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
10. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 2.0f. Crystal Impact, Bonn, Germany 1998.