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C–H···π and C–H···O Interactions in Coumarin 6 : 3-(2-benzothiazolyl)-7-(diethylamino)-coumarin

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Abstract— Crystal structure of coumarin 6 has been solved by X-ray diffraction. The crystals are triclinic, space group P-1, with a=8.823(2) Å, b=8.898(2) Å, c=11.025(9) Å, α=86.41(3)°, β=85.39(3)°, γ=76.23(3)°, Mr=350.42, V=837.1(3) Å^3, Z=2 and R=0.0516. The molecules are packed parallel to each other by weaker $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions. The detailed geometry of C–H$\cdots\pi$ interactions were discussed. The hydrogen bonds and non-traditional C–H···O interactions join the no-parallel molecules together. All the molecules packed wall-like with the molecular brick.

Keywords: *crystal structure, coumarin 6, π···π, C–H···π, C–H···O interactions, X-ray diffraction*

1. Introduction

Coumarins are relatively old molecules, the discovery of which dates back to the end of the 19th century. Coumarins are of interest because they constitute an important class of compounds, occupying a special place in nature and they form sub-units of many natural products. Coumarin and its derivatives are also widely used as additives in food, perfumes, cosmetics, pharmaceuticals, and agrochemicals[1,2].

Courmarins owe their commercial importance to their efficient light emission properties, their reasonable stability and their relative ease of synthesis. Coumarin fluorescent dyes are suitable for use in the coloration of synthetic fibers, in day light fluorescent pigments and in a range of applications which specifically exploit their light emission properties, including non-destructive flaw detection, tunable dye lasers and solar energy collectors. Coumarin 6, (3-(2-benzothiazolyl)-7-(diethylamino)-coumarin), is one of the most organic fluorescent materials with an electron-releasing group (N, N-diethylamino) in the 7-position and an electron-accepting heterocyclic group in the 3-position. There is some interest in the molecular design which could extend the available range of long-wavelength emitting fluorescent materials. The shift to longer wavelength has invariably been achieved by strengthening the electron-accepting character attached to the pyranone ring. The first single crystal of coumarin 6 was reported in 1995, in which the crystal data of it was investigated. In this paper, a single crystal of coumarin 6 with different packing model will be reported. Non-traditional C–H···O interactions were established in this crystal, which were not observed in the reported one. C–H···O interactions together with other interactions determined the packing model. It is helpful for us to understand and control the crystalline state and applied to the optical technologies.

2. Experimental

2.1 General Comments

Coumarin 6 is commercially available. And it can also be synthesized easily according to the reported methods[3]. Chemicals used for the synthesis were commercially available, were of AR grade,

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and were used as received without further purification. The yellow crystals of the title compound were obtained by slow evaporation of its solution in ethanol at room temperature. The crystalline solid product thus was separated by filtration, washed with ethanol and dried. Finally, single crystals suitable for X-ray diffraction were obtained.

2.2 Methodology

The crystal structure data collections was done on a ADSC Quantum 210 diffractometer using graphite synchrotron radiation (λ=0.76999 Å) at 293(2) K. A crystal with dimensions 0.20mm × 0.15mm × 0.10 mm was mounted on a glass fiber and detected. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement. The structure was solved by direct methods with program SHELXS-97 and refined by full matrix least squares on F^2 with SHELXL -97[4-6]. Direct phase determination yielded the positions of all non-hydrogen atoms. All non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically with C–H bond distances of 0.93–0.96 Å according to criteria described in the SHELXTL manual. The crystal used for the diffraction study showed no decomposition during data collection. A summary of the experimental and crystallographic data are presented in Table 1. Selected bond distances and angles can be seen in Table 2.

3. Results and Discussion

3.1 Geometry of the molecule

The molecular structure of coumarin 6 with atom numbering is given in Fig. 1. Crystal structure of coumarin 6 with triclinic(spacegroup*P*-1) has been reported[3]. In this paper, the space group of crystal coumarin 6 is same to the reported one with similar reference axes *a*, *b*, and *c*. However, the three angles between the axes are less than 90°, which is different from the reported crystal with two angle (α and β) larger than 90°. In this new crystal, the cormarin 6 crystallizes with two molecules per unit into triclinic crystal system with a space group of *P*-1. The bond lengths and bond angles of the two molecules in the crystal unit are all in the normal range. So the discussion can be limited to one of the molecules. According to the crystal structure, the coumarin ring and the benzothiazoly ring systems in the molecule are planar. The pyrone ring is deviated 2.44° compared to the thiazoly ring. Most of the basic data of this crystal is similar to the reported one. However, the interactions generated in this crystal are completely different from the reported one.

3.2 C–H···O interactions

The different intermolecular interactions lead to the different assembles in the crystal lattice. Only one kind of intermolecular hydrogen bond is observed in the crystal(Fig. 2). The adjacent nonparallel molecules are connected by intermolecular hydrogen

Table 1. Crystal data and structure refinement parameters

Bonds	Bond length (Å)	Bonds	Bond angle (Å)
N1—C7	1.307(2)	C7—N1—C1	110.5(1)
N1—C1	1.382(2)	C17—N2—C19	117.4(1)
N2—C14	1.365(2)	C6—S1—C7	88.9(1)
N2—C17	1.462(2)	N1—C1—C2	124.9(1)
N2—C19	1.466(2)	N1—C1—C6	115.1 (1)
O1—C9	1.213(2)	C5—C6—S1	129.1 (1)
O2—C12	1.379(2)	C1—C6—S1	109.6(1)
O2—C9	1.386(2)	N1—C7—S1	115.9(1)

Table 2. Selected bond lengths (Å) and angles (°)

Items	Data
Empirical formula	$C_{20}H_{18}N_2O_2S$
Formula weight	350.42
Temperature (K)	293(2)
Wavelength (Å)	0.76999
Crystal system	triclinic
Space group	*P-1*
Unit cell dimensions	a = 8.823(2) Å, b = 8.898(2) Å, c = 11.025(9) Å α = 86.41(3)°, β = 85.39(3)°, γ = 76.23(3)°
Volume	837.1(3) ($Å^3$)
Z	2
Calculated density	1.390g/cm^3
Absorption coefficient	0.21 cm^{-1}
F(000)	368
Crystal size	0.20 × 0.15 × 0.01 mm^3
Θ range for data collection	3.18 - 30.34°
Index ranges	$-11 \le h \le 10$, $-11 \le k \le 0$, $-14 \le l \le 14$
Reflections collected	3595
Independent reflections	3498
Completeness to θ = 25.50°	98.2%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3595/3498/228
Goodness-of-fit on F^2	1.112
Final R indices [I>2σ (I)]	R_1 = 0.0516, wR_2 = 0.1670
R indices (all data)	R_1 = 0.0522, wR_2 = 0.1679
Largest diff. peak and hole	0.388 and -0.670 e$Å^{-3}$

bonds (C20–H20B··· $N1^{i1}$, i1: x, y, z). The interactions that can not be neglected are the weak C–H···O interactions, which are different from the traditional C–H···O hydrogen bonds (Fig. 3). Totally four kinds of C–H···O interactions are generated in the crystals : C18–H18B···$O1^{i2}$(i2: x, y, 1+z), C18–H18B···$O2^{i2}$, C5–H5···$O1^{i3}$(i3: –1+x, 1+y, z), C19–H19B···$O1^{i3}$ (Fig. 3). The distance of H···O are 2.941(1) Å (H18B···$O1^{i2}$), 2.697(1) Å (H18B···$O21^{i2}$), 2.760(2) Å (H5···$O1^{i3}$), and 2.624(1) Å (H19B···$O1^{i3}$).

The C···O contacts in this crystal range from 3.17 to 3.71 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[7,8]. All of the C–H···O angles ranged from 115.9° to 147.3°, which are also in agreement with Desiraju's findings.

3.3 π···π and C-H···π interactions

The molecules are packaged parallel to each other and are stacked layer by layer (Fig. 4). π··· π interactions and C–H···π interactions join the

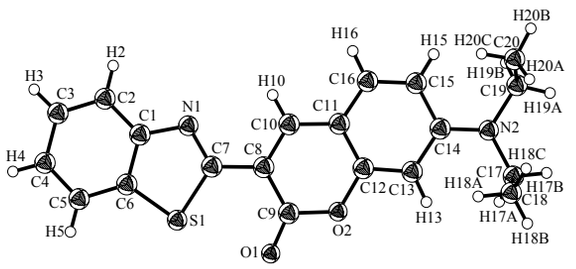

Fig. 1. ORTEP drawing of the coumarin 6 with displacement ellipsoids plotted at 50% probability level.

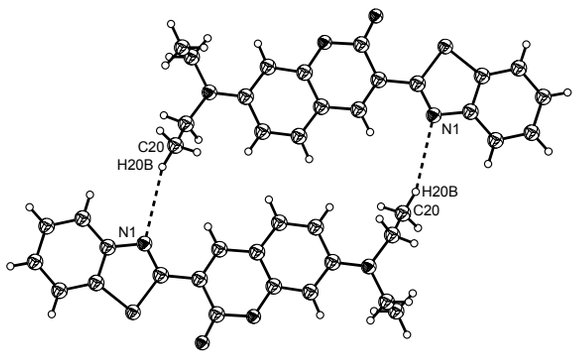

Fig. 2. Partial packing diagram of the coumarin 6 with hydrogen bonds drawn as dashed lines.

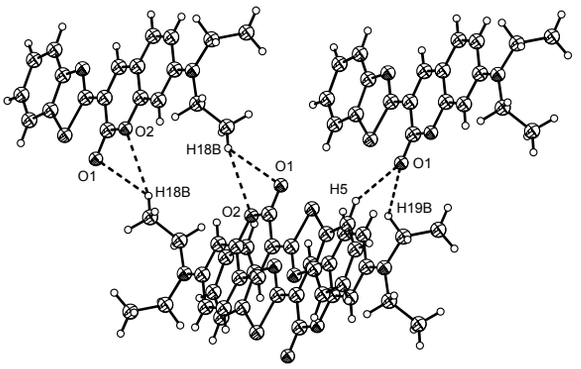

Fig. 3. Partial packing diagram of the coumarin 6 with C–––H···O interaction drawn as dashed lines.

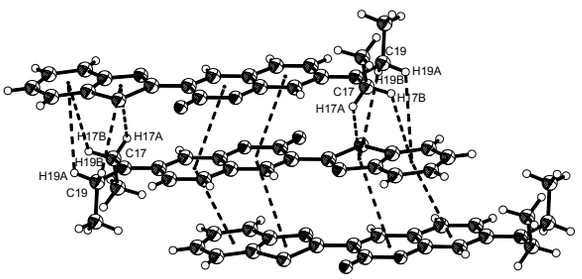

Fig. 4. Partial packing diagram of the title compound with π···π and C–H···π interaction drawn as dashed lines.

Table 3. C–H···π interactions geometry (Å, °)

Geometry	$d_{H\cdots\pi}$	θ	α	$d=d_{H\cdots\pi}\cos\theta$	Type
C17–H17A···Cg1^{i5}	3.501	55.5	99.9	1.985	
C17–H17A···Cg2^{i6}	3.624	53.3	88.6	2.166	Type VI
C17–H17B···Cg1^{i5}	3.774	55.0	83.6	2.166	Type VI
C17–H17B···Cg2^{i6}	3.167	77.2	118.4	0.703	Type III
C19–H19A···Cg1^{i5}	3.809	55.1	81.4	2.178	Type VI
C19–H19A···Cg2^{i6}	3.471	63.3	116.1	1.561	Type V
C19–H19B···Cg1^{i5}	3.464	55.0	102.1	1.987	Type V
C19–H19B···Cg2^{i6}	3.988	45.0	83.3	2.822	Type VI
C10–H10···Cg3^{i7}	3.889	58.9	66.3	2.007	Type VI
C16–H16···Cg4^{i7}	3.909	57.8	65.8	2.080	Type VI
C4–H4···Cg3^{i7}	3.802	68.2	71.3	1.414	Type VI
C5–H5···Cg3^{i7}	3.736	72.4	72.4	1.128	Type VI
C10–H10···Cg1^{i7}	3.747	66.5	67.1	1.495	Type VI

molecules parallel to each other. Obviously π···π interactions were found between parallel molecules. The centroid–centroid (C8/C10/C11/C12/O2/C9 and C11/C12/C13/C14/C15/C16) distance is 3.632(1) Å and the angle between the ring normal and the vectors of two interacted ring centroid is 67.4(1)°. The shorter atom atom contact between the two parallel plane is 3.331(3) Å (C10 to C12^{i4}, i4:

2-x, 1-y, 1-z), characteristic of a weak interaction[9]. Other π···π interactions are $\pi_{C11-C16}\cdots\pi_{C1-C6}$ and $\pi_{C11-C16}\cdots\pi_{C8-C12/O2}$ with the centroid–centroid distances of 3.773(1) Å and 3.527(1) Å. The π···π interaction display the usual slipped stacking geometry, with the interacting π system parallel displaced. The distance between the adjacent parallel molecules are 3.326(2) Å and 3.474(2) Å, respectively.

There are thirteen C–H···π intermolecular interactions, involving eight hydrogen atoms and the π electron system of the four rings (Table 3).

A typical C–H···π interaction observed in the crystal is C17–H17B···Cg1^{i5}(Cg1-centroid of ring C1/C6/S1/C7/N1, i5: -x, -y, 1-z). The hydrogen atom is directly above the centre of the heterocyclic ring, but the C–H bond points towards a ring carbon. The geometry of this interaction corresponds to type III[10].

In another two bond, C19---H19A··· Cg2$^{i6\backslash}$ (Cg2-centroid of ring C1/C2/C3/ C4/C5/C6, i6: -x, 1-y, 1-z) and C19---H19B···Cg1^{i5}, the hydrogen atoms interact with a carbon at the edge of the acceptor ring (typeV).

In the remaining C–H···π interactions, the direct of C–H bond indicates that it points away from the ring although the hydrogen is close to a carbon (typeVI).

(Symmetry codes i5: -x, -y, 1-z; i6: -x, 1-y, 1-z; i7: x, y, z; Cg1-centroid of ring C1/C6/S1/C7/N1, Cg2-centroid of ring C1/C2/C3/C4/C5/C6, Cg3-centroid of ring C11/C12/C13/C14/C15/C16, Cg4-centroid of ring C9/C10/C11/C12/O2, definition of geometric parameters according to [10])

4. Conclusions

In conclusion, the single crystal of coumarin 6 was obtained and the structure was solved. Traditional π···π interactions and C–H···π interactions were established in the crystal, by which the molecules were packed parallel to each other. Unusual interactions, C–H···O interactions, were found in the crystal lattice, which is different from the traditional hydrogen bonds of H···O. Only one kind of hydrogen bond was found. And the molecules were joined into network by them.

Although parallel molecules are found in the crystal, the molecules are not packed layer by layer. The crystal is packed like the wall, in which the molecules is bricklike and they are bricked by various kinds of intermolecular interactions.

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