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X-ray Structure Analysis Online

Crystal Structure of a Linear Carbazole-Coumarin Hybrid Dye

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The crystal structure of 10*H*-4-methyl-2*H*-2-oxopyrano[5,6-*b*]carbazole hydrate was determined by X-ray diffraction. The crystal, $2C_{16}H_{11}NO_2{\cdot}H_2O$, belongs to space group $P2_1/a$ with cell dimensions of a = 7.927(6)Å, b = 22.78(1)Å, c = 13.73(1)Å, β = 102.31(2)°. The final R value is 0.061 for 4651 reflections ($I > 2.00\sigma(I)$). There are two independent coumarin molecules (A, B) and one water molecule in an asymmetric unit. Molecules A and B are linked through the N–H···O=C and the C=O···H–O(water)···H–N hydrogen bondings to form a cyclic hetero dimer.

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Coumarin derivatives are of great interest, because they are widely used as laser dyes[1] and fluorescent brightners.[2] We have reported on the crystal structure of 4-methyl-4′,5′-dihydropyrrolocoumarin.[3] In this work, an X-ray structural analysis of 10*H*-4-methyl-2*H*-2-oxopyrano[5,6-*b*]carbazole hydrate (I, see Figs. 1 and 2) was carried out in order to clarify the effect of extending the π-conjugation to the coumarin moiety on the ground-state molecular structure. This tetracyclic compound is regarded as a carbazole-coumarin hybrid in that a carbazole moiety is condensed with a 2-pyrone skeleton.

10*H*-4-Methyl-2*H*-2-oxopyrano[5,6-*b*]carbazole was synthesized in the following manner:[4] a mixture of 1.0 g (5.5 mmol) of 2-hydroxycarbazole, 3.5 g (15 mmol) of ethyl acetoacetate and 1.7 g (13 mmol) of anhydrous $ZnCl_2$ was refluxed at 120°C in 6 ml of dry ethanol for 8 h. The reaction mixture was poured into cold 0.1 M hydrochloric acid. The crude product was filtered off, dried *in vacuo* and put on a chromatography column packed with silica gel and eluted with a hexane/ethyl acetate mixture (1/1) (recrystallized from $CHCl_3$): Yield 15%; Mp 277 – 278°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.55 (1H, s), 8.22 – 8.21 (1H, d), 7.57 – 7.25 (4H, m), 6.18 (1H, s), 2.61 (3H, s); MS m/z = 249 (M^+); IR (KBr, cm^{-1}) 3254, 3088, 1844, 1707, 1645, 1615, 1586, 1571, 1506, 1496, 1478, 1452; UV (λ_{max}/nm ($\varepsilon/10^4$ M^{-1} cm^{-1}), C_2H_5OH) 365 (2.2), 309 (3.7), 279 (2.5), 229 (4.4); Found: C, 76.93; H, 4.48; N, 5.57%. Calcd for $C_{16}H_{11}NO_2$: C, 77.09; H, 4.44; N, 5.61%.

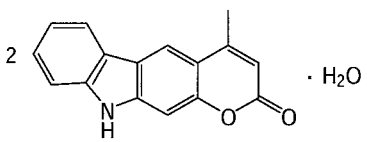

Fig. 1 Chemical structure of I.

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Colorless crystals of I suitable for X-ray diffraction analysis were obtained by the slow evaporation of an aqueous acetonitrile solution at room temperature. Data collections were performed at 123 K. All measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo K_α radiation (λ = 0.7107 Å). The data

Table 1 Crystal and experimental data

Formula: $2C_{16}H_{11}NO_2{\cdot}H_2O$
Formula weight: 516.55
Crystal system: monoclinic
a = 7.927(6)Å
b = 22.78(1)Å
c = 13.73(1)Å
β = 102.31(2)°
V = 2423(2)Å^3
Space group: $P2_1/a$ Z = 4
D_{calc} = 1.416 g/cm^3
F(0 0 0) = 1080.00
μ(Mo K_α) = 0.96 cm^{-1}
T = 123 K
$2\theta_{max}$ = 60.7° with Mo K_α (0.7107 Å)
No. observations = 4651 ($I > 2.00\sigma(I)$)
No. variables = 368
R, Rw = 0.061, 0.076
Goodness-of-fit = 1.55
$(\Delta/\sigma)_{max}$ = 0.000
$(\Delta\rho)_{max}$ = 0.68 e$^-$/Å^3
$(\Delta\rho)_{min}$ = –0.62 e$^-$/Å^3
Diffractometer: Rigaku/MSC Mercury CCD
Program system: teXsan
Structure determination: direct method (MULTAN88)
Refinement: full-matrix least-squares

CCDC 606661 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

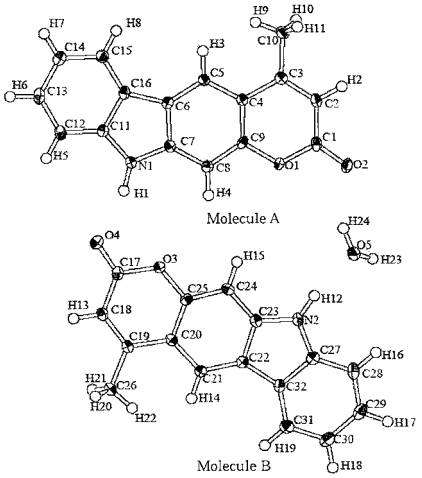

Fig. 2 Molecular structure of I along with the labeling atoms. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level.

were corrected for Lorentz-polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located by a difference Fourier synthesis and a geometrical calculation, with the H atoms bonded to N(1), N(2), and O(5) atoms also being refined isotropically. All calculations were performed using the teXsan crystallographic software package.

Table 1 lists the crystal data and the experimental conditions. Figure 2 illustrates an ORTEP diagram of the molecule with the atomic-labeling scheme. The final position parameters are given in Table 2.

There are two independent coumarin molecules (A, B) and one water molecule per asymmetric unit. Molecules A and B are linked through the N–H···O=C and the C=O···H–O(water)···H–N hydrogen bondings to form a cyclic hetero dimer. [N(1)···O(4) 2.830(2)Å, N(1)–H···O(4) 158(2)˚; N(2)···O(5) 2.807(2)Å, N(2)–H···O(5) 163(2)˚; O(5)···O(2) 2.858(3)Å, O(5)–H···O(2) 161(3)˚; O(5)···O(2)^{i} 2.959(2)Å, O(5)–H···O(2)^{i} 170(3)˚; symmetry code i] $x + 1/2, -y + 1/2, z$].

Molecule A and B have similar molecular geometries to each other. The carbazole moieties are coplanar with the other molecules. The sum of the bond angles around the N(1) and N(2) atoms is 358˚. This value indicates that these nitrogen atoms are almost sp^2-hybridized. The geometries of the aromatic rings can be compared with that of bicyclic coumarins.[5] The C(6)–C(7) [1.426(3)Å] and the C(22)–C(23) [1.428(3)Å] bonds are clearly longer than the corresponding average value for bicyclic coumarins (1.397 Å).[5]

The angles of C(6)–C(7)–C(8) [122.0(2)˚] and C(22)–C(23)–C(24) [121.8(2)˚] are slightly larger than the corresponding average value for bicyclic coumarins (120.9˚).[5]

Table 2 Atomic coordinates and equivalent isotropic thermal parameters (B_{eq})

atom	x	y	z	B_{eq}(Å^2)
O(1)	0.2875(2)	0.11136(6)	0.6796(1)	1.54(3)
O(2)	0.3374(2)	0.20669(6)	0.6923(1)	1.88(3)
O(3)	0.6112(2)	-0.07960(6)	0.8025(1)	1.70(3)
O(4)	0.4680(2)	-0.16269(7)	0.7719(1)	2.34(3)
O(5)	0.6910(2)	0.19718(7)	0.7934(1)	2.12(4)
N(1)	0.1813(2)	-0.09714(7)	0.6696(1)	1.62(4)
N(2)	0.9190(2)	0.10431(8)	0.8600(1)	1.58(4)
C(1)	0.2288(3)	0.16784(9)	0.6691(2)	1.57(4)
C(2)	0.0474(3)	0.17721(9)	0.6321(2)	1.66(4)
C(3)	-0.0663(3)	0.13232(9)	0.6089(2)	1.51(4)
C(4)	-0.0029(3)	0.07285(9)	0.6220(2)	1.37(4)
C(5)	-0.1091(3)	0.02328(9)	0.6009(1)	1.42(4)
C(6)	-0.0389(3)	-0.03226(9)	0.6175(1)	1.35(4)
C(7)	0.1419(3)	-0.03839(9)	0.6567(2)	1.42(4)
C(8)	0.2512(3)	0.00966(9)	0.6751(2)	1.50(4)
C(9)	0.1756(3)	0.06421(9)	0.6585(1)	1.38(4)
C(10)	-0.2544(3)	0.14433(9)	0.5698(2)	1.85(4)
C(11)	0.0311(3)	-0.12961(9)	0.6396(2)	1.48(4)
C(12)	0.0104(3)	-0.19004(9)	0.6402(2)	1.72(4)
C(13)	-0.1533(3)	-0.21217(9)	0.6025(2)	1.84(4)
C(14)	-0.2936(3)	-0.17531(10)	0.5670(2)	1.88(4)
C(15)	-0.2732(3)	-0.11454(9)	0.5693(2)	1.72(4)
C(16)	-0.1090(3)	-0.09125(9)	0.6056(2)	1.44(4)
C(17)	0.6091(3)	-0.13986(9)	0.8009(2)	1.72(4)
C(18)	0.7697(3)	-0.16999(9)	0.8326(2)	1.66(4)
C(19)	0.9218(3)	-0.14139(9)	0.8627(2)	1.42(4)
C(20)	0.9230(3)	-0.07777(9)	0.8619(1)	1.35(4)
C(21)	1.0734(3)	-0.04403(9)	0.8882(1)	1.42(4)
C(22)	1.0626(3)	0.01691(9)	0.8848(1)	1.41(4)
C(23)	0.8976(3)	0.04443(9)	0.8565(2)	1.51(4)
C(24)	0.7468(3)	0.01207(9)	0.8294(2)	1.54(4)
C(25)	0.7634(3)	-0.04829(9)	0.8318(2)	1.42(4)
C(26)	1.0856(3)	-0.17507(9)	0.8981(2)	1.71(4)
C(27)	1.0943(3)	0.11693(9)	0.8880(2)	1.62(4)
C(28)	1.1754(3)	0.17134(9)	0.9002(2)	1.86(4)
C(29)	1.3538(3)	0.17203(10)	0.9283(2)	2.10(5)
C(30)	1.4491(3)	0.1200(1)	0.9431(2)	2.20(5)
C(31)	1.3675(3)	0.06581(10)	0.9315(2)	1.86(4)
C(32)	1.1883(3)	0.06400(9)	0.9045(1)	1.42(4)

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

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