Crystal Structure of an Angular Carbazole-Coumarin Hybrid Dye

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The crystal structure of 7*H*-4-methyl-2*H*-2-oxopyrano[5,6-*c*]carbazole has been determined by X-ray diffraction. The crystal, $C_{16}H_{11}NO_2$, belongs to space group *C*2/*c* with cell dimensions of a = 17.29(2)Å, b = 7.398(7)Å, c = 19.09(4)Å, β = 105.36(3)°. The final R value is 0.056 for 2257 reflections ($I > 2.00\sigma(I)$). The C=O and the NH groups of neighboring molecules are linked through intermolecular hydrogen bondings to form an infinite chain structure.

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Coumarin derivatives containing a rigid amino-moiety, such as a julolidine ring, are used as efficient laser dyes. The crystal structures have been solved for this kind of laser dye.[1,2] In this paper we report on the crystal structure of 7*H*-4-methyl-2*H*-2-oxopyrano[5,6-*c*]carbazole (I, see Figs. 1 and 2). This tetracyclic compound can be regarded as a rigidized aminocoumairn consisting of carbazole and coumarin moieties. It is interesting to compare the molecular geometries of linear and angular carbazole-coumarin hybrids.[3] Compound I was synthesized in the following manner:[4] a mixture of 1.1 g (6.0 mmol) of 4-hydroxycarbazole purified by column chromatography packed with silica gel and eluted with a hexane/ethyl acetate mixture (4/1), 2.7 g (20 mmol) of ethyl acetoacetate, and 1.1 g (8.4 mmol) of anhydrous $ZnCl_2$ was

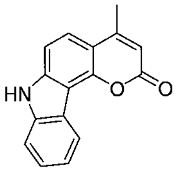

Fig. 1 Chemical structure of I.

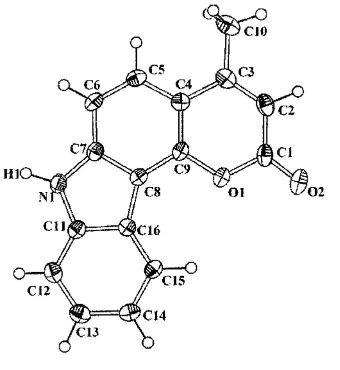

Fig. 2 Molecular structure of I along with the labeling atoms. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level.

Table 1 Crystal and experimental data

Formula: $C_{16}H_{11}NO_2$
Formula weight: 249.27
Crystal system: monoclinic
a = 17.29(2)Å
b = 7.398(7)Å
c = 19.09(4)Å
β = 105.36(3)°
V = 2354(5)Å^3
Space group: *C*2/*c* Z = 8
D_{calc} = 1.407 g/cm^3
$F(0\ 0\ 0)$ = 1040.00
μ(Mo K_α) = 0.94 cm^{-1}
T = 123 K
$2\theta_{max}$ = 60.5° with Mo K_α (0.71070 Å)
No. observations = 2257 ($I > 2.00\sigma(I)$)
No. variables = 215
R, Rw = 0.056, 0.069
Goodness-of-fit = 1.34
$(\Delta/\sigma)_{max}$ = 0.000
$(\Delta\rho)_{max}$ = 0.38 e$^-$/Å^3
$(\Delta\rho)_{min}$ = –0.28 e$^-$/Å^3
Diffractometer: Rigaku/MSC Mercury CCD
Program system: teXsan
Structure determination: direct method (SHELXS86)
Refinement: full-matrix least-squares

CCDC 607187 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.

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

Atom	x	y	z	B_{eq}(Å^2)
O(1)	0.52797(8)	0.2474(2)	0.43857(7)	2.07(3)
O(2)	0.65003(9)	0.1449(2)	0.44854(9)	3.24(3)
N(1)	0.27690(10)	0.5018(2)	0.39837(9)	2.14(3)
C(1)	0.5983(1)	0.1733(3)	0.4801(1)	2.32(4)
C(2)	0.6029(1)	0.1351(3)	0.5548(1)	2.42(4)
C(3)	0.5424(1)	0.1703(3)	0.5852(1)	2.19(4)
C(4)	0.4699(1)	0.2530(2)	0.5411(1)	1.88(3)
C(5)	0.4034(1)	0.3016(3)	0.5674(1)	2.13(4)
C(6)	0.3369(1)	0.3851(3)	0.5246(1)	2.13(4)
C(7)	0.3351(1)	0.4188(3)	0.4517(1)	1.91(3)
C(8)	0.3986(1)	0.3664(2)	0.42241(10)	1.74(3)
C(9)	0.4659(1)	0.2882(2)	0.4684(1)	1.76(3)
C(10)	0.5487(2)	0.1229(3)	0.6631(1)	2.90(4)
C(11)	0.3006(1)	0.5038(3)	0.3344(1)	1.98(3)
C(12)	0.2620(1)	0.5764(3)	0.2670(1)	2.34(4)
C(13)	0.2979(1)	0.5547(3)	0.2111(1)	2.49(4)
C(14)	0.3711(1)	0.4630(3)	0.2212(1)	2.32(4)
C(15)	0.4110(1)	0.3959(3)	0.2891(1)	2.02(4)
C(16)	0.3762(1)	0.4174(2)	0.34639(10)	1.78(3)

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

Table 3 Selected bond lengths (Å), bond angles (˚) and torsion angles (˚)

C(4)	C(5)	1.417(3)	C(5)	C(6)	1.370(3)
C(6)	C(7)	1.406(3)	C(7)	C(8)	1.411(3)
C(8)	C(9)	1.385(3)	C(4)	C(9)	1.394(3)
C(8)	C(16)	1.449(3)	C(11)	C(12)	1.392(3)
C(11)	C(16)	1.418(3)	C(12)	C(13)	1.378(3)
C(13)	C(14)	1.404(3)	C(14)	C(15)	1.388(3)
C(15)	C(16)	1.390(3)	N(1)	C(7)	1.372(3)
N(1)	C(11)	1.386(3)			

C(5)	C(4)	C(9)	118.3(2)	C(4)	C(5)	C(6)	122.3(2)
C(5)	C(6)	C(7)	117.7(2)	C(6)	C(7)	C(8)	121.9(2)
C(7)	C(8)	C(9)	118.3(2)	C(4)	C(9)	C(8)	121.4(2)
C(9)	C(8)	C(16)	134.4(2)	C(7)	C(8)	C(16)	107.2(2)
C(12)	C(11)	C(16)	121.3(2)	C(8)	C(16)	C(11)	105.6(2)
C(8)	C(16)	C(15)	134.6(2)	C(11)	C(16)	C(15)	119.8(2)
C(7)	N(1)	C(11)	109.1(2)	N(1)	C(7)	C(8)	108.9(2)
N(1)	C(7)	C(6)	129.2(2)	N(1)	C(11)	C(12)	129.6(2)
N(1)	C(11)	C(16)	109.2(2)	C(7)	N(1)	H	121(1)
C(11)	N(1)	H	129(1)				

C(4)	C(9)	C(8)	C(16)	-179.4(2)	C(4)	C(5)	C(6)	C(7)	1.4(3)
C(9)	C(8)	C(16)	C(15)	5.7(4)	N(1)	C(7)	C(8)	C(9)	176.6(2)
N(1)	C(7)	C(8)	C(16)	-1.4(2)	C(8)	C(7)	N(1)	C(11)	0.5(2)
C(7)	N(1)	C(11)	C(12)	-178.6(2)	C(7)	N(1)	C(11)	C(16)	0.7(2)
N(1)	C(7)	C(6)	C(5)	-178.9(2)	N(1)	C(11)	C(12)	C(13)	-178.0(2)
N(1)	C(11)	C(16)	C(8)	-1.5(2)	N(1)	C(11)	C(16)	C(15)	177.3(2)
C(6)	C(7)	N(1)	C(11)	-179.5(2)	C(8)	C(16)	C(15)	C(14)	179.5(2)

Estimated standard deviations in the least significant figure are given in parentheses.

refluxed at 120˚C in 7 ml of dry ethanol for 24 h. The reaction mixture was poured into cold water. 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 ethyl acetate): Yield 11%; Mp over 300˚C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.47 – 8.46 (1H, d), 7.78 – 7.33 (5H, m), 6.22 (1H, s), 2.57 (3H, s); MS m/z = 249 (M^+); IR (KBr, cm^{-1}) 3257, 2991, 1704, 1633, 1599, 1562, 1497, 1486, 1450; UV (λ_{max}/nm ($\varepsilon/10^4$ M^{-1} cm^{-1}), C_2H_5OH) 352 (1.4), 284 (2.5), 237 (3.0), 215 (3.2); Found: C, 76.94; H, 4.49; N, 5.58%. Calcd for $C_{16}H_{11}NO_2$: C, 77.09; H, 4.44; N, 5.61%.

Colorless crystals of I suitable for X-ray diffraction analysis were obtained by slow evaporation of an ethyl acetate 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 = 0.71070 Å). The data 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 refined isotropically. All calculations were performed using the teXsan crystallographic software package.

Table 1 lists the crystal data and experimental conditions. Figure 2 is an ORTEP diagram of the molecule with the atomic-labeling scheme. The final position parameters are given in Table 2, and selected bond lengths, bond angles and torsion angles are listed in Table 3. The C=O and the NH groups of neighboring molecules are linked through intermolecular hydrogen bondings to form an infinite chain structure [N(1)···O(2)^i 2.822(3)Å, N(1)–H···O(2)^i 167(2)˚; symmetry code i) x–1/2, y+1/2, z].

The carbazole moiety in I is almost coplanar with the pyrone ring in I. The sum of the bond angles around N(1) is 359˚. This value indicates that the nitrogen is almost sp^2-hybridized. The geometry of an aromatic ring can be compared with that of bicyclic coumarins.[5] The C(7)–C(8) bond [1.411(3)Å] is clearly longer than the corresponding average value for bicyclic coumarins (1.386 Å).[5] The angle of C(6)–C(7)–C(8) [121.9(2)˚] in I is slightly larger than the corresponding average value for bicyclic coumarins (120.9˚).[5]

References

1. T. Honda, I. Fujii, N. Hirayama, N. Aoyama, and A. Miike, *Acta Cryst.*, **1996**, *C52*, 364.
2. T. Honda, I. Fujii, N. Hirayama, N. Aoyama, and A. Miike, *Acta Cryst.*, **1996**, *C52*, 2363.
3. T. Fukagawa, N. Kitamura, S. Kohtani, S. Kitoh, K.-K. Kunimoto, and R. Nakagaki, *Anal. Sci.*, **2006**, *22*, x191.
4. E. R. Bissell, D. K. Larson, and M. C. Croudace, *J. Chem. Eng. Data*, **1981**, *26*, 348.
5. N. Kitamura, S. Kohtani, and R. Nakagaki, *J. Photochem., Photobiol., C: Rev.*, **2005**, *6*, 168.