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X-ray Structure Analysis Online

Crystal Structure of a Coumarin-Indoline Hybrid Dye

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The crystal structure of 4-methyl-4′,5′-dihydropyrrolocoumarin (MDPC) has been determined by X-ray diffraction. The crystal, $C_{12}H_{11}NO_2$, belongs to space group $P2_1/c$ with cell dimensions of a = 7.539(2)Å, b = 19.230(2)Å, c = 6.9395(9)Å, β = 103.89(1)˚. The final R value is 0.036. The methylene bridge in the indoline moiety makes the amino moiety more pyramidal than simple *N*-alkylation.

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In this paper we report on the crystal structure of 4-methyl-4′,5′-dihydropyrrolocoumarin (MDPC, see Figs. 1 and 2). The tricyclic chromophore is formed on ring-closure by bridging amino nitrogen (N(1)) and ring carbon (C(6)) with two methylene groups (C(7) and C(8)). The tricyclic compound is regarded as a coumarin-indoline hybrid in which a pyrrolidine moiety is condensed with a coumarin skeleton.

A previous spectroscopic study[1] suggests that the methylene bridge makes the amino moiety more pyramidal than simple *N*-alkylation without ring formation. Pyramidalization at the nitrogen atom may be responsible for the observed blue shift and the slight decrease in the molar extinction coefficient or oscillator strength in comparison with the more planar *N*-alkylaminocoumarin.[1]

MDPC was synthesized according to a procedure described by Quanten *et al.*[2] A yellow plate crystal of the MDPC, having approximate dimensions of 0.10 × 0.15 × 0.20 mm, was mounted on a glass fiber. Data collections were performed at 295 K with graphite monochromated Cu K_α radiation (λ =

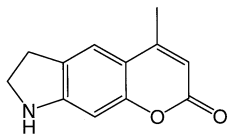

Fig. 1 Chemical structure of MDPC.

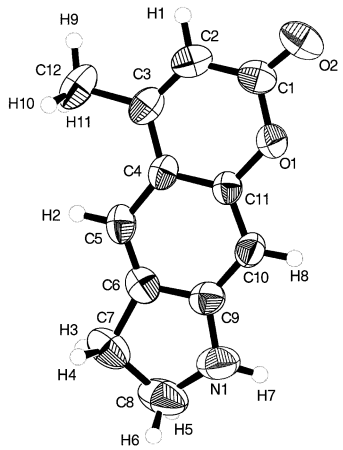

Fig. 2 Molecular structure of MDPC along with the labeling atoms. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level.

Table 1 Crystal and experimental data

Formula: $C_{12}H_{11}NO_2$
Formula weight: 201.22
Crystal color, habit: yellow, plates
Crystal size: 0.10 × 0.15 × 0.20 mm
Crystal system: monoclinic
a = 7.539(2)Å
b = 19.230(2)Å
c = 6.9395(9)Å
β = 103.89(1)˚
V = 976.7(3)Å^3
Space group: $P2_1/c$ Z = 4
D_{calc} = 1.368 g/cm^3
F(0 0 0) = 424.00
μ(Cu K_α) = 7.66 cm^{-1}
T = 295 ± 1 K
$2\theta_{max}$ = 149.9˚ with Cu K_α (1.54178 Å)
No. observations = 1981 (All, 2θ < 149.9˚)
No. variables = 181
R, Rw = 0.036, 0.109
Goodness of fit = 1.02
$(\Delta/\sigma)_{max}$ = 0.00
$(\Delta\rho)_{max}$ = 0.18 e$^-$/Å^3
$(\Delta\rho)_{min}$ = –0.12 e$^-$/Å^3
Diffractometer: Rigaku AFC7R(rotating anode)
Program system: teXsan
Structure determination: direct method (SAPI91)
Refinement: full-matrix least-squares (SHELXL-97)

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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)	0.0722(1)	0.08188(5)	0.1988(1)	4.21(2)
O(2)	-0.0471(2)	0.18565(6)	0.1305(2)	6.23(3)
N(1)	0.3030(2)	-0.15052(7)	0.3223(3)	5.90(4)
C(1)	0.0380(2)	0.14741(8)	0.2596(2)	4.45(3)
C(2)	0.1064(2)	0.16294(8)	0.4646(3)	4.69(3)
C(3)	0.1959(2)	0.11562(8)	0.5967(2)	4.27(3)
C(4)	0.2261(2)	0.04686(7)	0.5306(2)	3.58(3)
C(5)	0.3148(2)	-0.00815(8)	0.6530(2)	4.11(3)
C(6)	0.3342(2)	-0.07152(8)	0.5746(2)	4.22(3)
C(7)	0.4214(3)	-0.1383(1)	0.6679(3)	5.71(4)
C(8)	0.3693(3)	-0.1914(1)	0.5011(4)	7.28(6)
C(9)	0.2676(2)	-0.08362(7)	0.3705(2)	4.22(3)
C(10)	0.1821(2)	-0.03170(8)	0.2451(2)	4.14(3)
C(11)	0.1621(2)	0.03211(7)	0.3284(2)	3.45(2)
C(12)	0.2655(4)	0.1343(1)	0.8119(3)	6.19(5)
H(1)	0.079(2)	0.2097(10)	0.503(3)	5.699(5)
H(2)	0.358(2)	0.0018(9)	0.792(3)	5.183(5)
H(3)	0.378(3)	-0.150(1)	0.786(3)	7.452(7)
H(4)	0.556(3)	-0.1324(9)	0.712(3)	6.348(5)
H(5)	0.275(4)	-0.222(1)	0.520(3)	9.263(8)
H(6)	0.475(3)	-0.221(1)	0.489(3)	7.717(7)
H(7)	0.226(3)	-0.168(1)	0.210(3)	7.962(8)
H(8)	0.133(2)	-0.0399(9)	0.107(3)	4.940(4)
H(9)	0.231(3)	0.181(1)	0.836(4)	8.979(8)
H(10)	0.403(3)	0.130(1)	0.853(3)	7.432(7)
H(11)	0.215(3)	0.103(1)	0.893(4)	8.861(8)

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

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

O(1)	C(1)	1.373(2)	O(2)	C(1)	1.216(2)		
C(1)	C(2)	1.424(2)	C(2)	C(3)	1.351(2)		
C(3)	C(4)	1.436(2)	C(4)	C(5)	1.419(2)		
C(5)	C(6)	1.357(2)	C(6)	C(9)	1.404(2)		
C(9)	C(10)	1.379(2)	C(10)	C(11)	1.380(2)		
O(1)	C(11)	1.375(2)	C(4)	C(11)	1.399(2)		
C(6)	C(7)	1.515(2)	C(7)	C(8)	1.523(3)		
N(1)	C(8)	1.452(3)	N(1)	C(9)	1.372(2)		
C(4)	C(5)	C(6)	120.7(1)	C(5)	C(6)	C(9)	120.4(1)
C(6)	C(9)	C(10)	121.1(1)	C(9)	C(10)	C(11)	117.5(1)
C(5)	C(6)	C(7)	131.9(1)	C(7)	C(6)	C(9)	107.7(1)
C(6)	C(7)	C(8)	103.7(2)	N(1)	C(8)	C(7)	105.0(2)
C(8)	N(1)	C(9)	110.3(2)	N(1)	C(9)	C(6)	111.0(1)
N(1)	C(9)	C(10)	127.9(2)	C(8)	N(1)	H(7)	123(1)
C(9)	N(1)	H(7)	115(1)				
C(4)	C(5)	C(6)	C(7)	179.9(2)	C(4)	C(5)	C(6)	C(9)	0.4(2)
C(5)	C(6)	C(7)	C(8)	171.7(2)	N(1)	C(9)	C(6)	C(5)	179.3(1)
N(1)	C(8)	C(7)	C(6)	14.0(2)	C(7)	C(8)	N(1)	C(9)	-15.1(2)
C(8)	N(1)	C(9)	C(10)	-171.1(2)	C(6)	C(9)	N(1)	C(8)	9.9(2)
N(1)	C(9)	C(10)	C(11)	-179.9(2)	N(1)	C(9)	C(6)	C(7)	-0.3(2)
C(6)	C(9)	C(10)	C(11)	-1.0(2)	C(8)	C(7)	C(6)	C(9)	-8.8(2)
C(7)	C(6)	C(9)	C(10)	-179.3(2)					

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

1.54178 Å) and a rotating anode generator on a Rigaku AFC7R diffractometer. 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. 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 illustrates 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 bond lengths in MDPC are in good agreement with those observed in other 7-aminocoumarins and *N*-alkylaminocoumarins.[3-5] The sum of bond angles around N(1) is 348˚. This value indicates that the nitrogen is neither purely sp^3-hybridized nor purely sp^2-hybridized. The sum of the bond angles in MDPC (348˚) is smaller than the corresponding value, *ca*. 360˚ in *N*,*N*-dialkylated coumarins.[3-5] While the plane defined by a dimethylamino group in coumarin 152[3,4] or coumarin 311[5] is coplanar with the molecular plane of coumarin, the amino moiety in MDPC is pyramidal, and not coplanar with the rest of the molecules. The absolute values of the following torsion angles are clearly different from 0˚ or 180˚: C(5)–C(6)–C(7)–C(8)–N(1)–C(9), C(7)–C(8), C(6)–C(7)–C(8)–N(1), C(6)–C(9)–N(1)–C(8), C(8)–N(1)–C(9)–C(10), and C(8)–C(7)–C(6)–C(9). These results show that C(8) is completely deviated from the molecular plane of coumarin.

The present findings are in accordance with the conclusion obtained by spectroscopic analysis.[1]

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