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6,7,8,9-Tetrahydro-4-trifluoromethyl-2*H*-pyrano[3,2-*g*]quinolin-2-one, (I), and 6,7,8,9-Tetrahydro-9-ethyl-4-trifluoromethyl-2*H*-pyrano[3,2-*g*]quinolin-2-one, (II)

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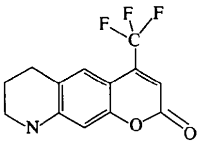
Abstract

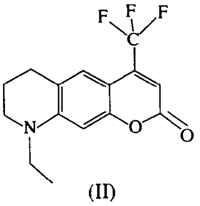
The title compound, $C_{13}H_{10}F_3NO_2$, (I), and its ethyl derivative, $C_{15}H_{14}F_3NO_2$, (II), are trifluoromethylcoumarin derivatives of the 6,7,8,9-tetrahydro-2*H*-pyrano[3,2-*g*]quinolin-2-one moiety. Compound (I) is stabilized by one C—F···H and two C—O···H intermolecular hydrogen bonds. Compound (II) crystallizes with two molecules in the asymmetric unit and is stabilized by van der Waals intermolecular interactions. The independent molecules in (II) are stacked in parallel layers in an alternating sequence, with the coumarin moieties forming an angle of 76.5 (4)° between adjacent parallel stacks.

Comment

Both title compounds are laser dyes and are also known as coumarin 340, (I), and coumarin 355, (II). Few examples of coumarin derivatives involving a fused piperazine ring system adjacent to the coumarin moiety which are used as laser dyes have been crystallized and structurally characterized.



(I)



(II)

Bond lengths and angles in the coumarin moiety of each compound are normal (Jasinski & Woudenberg, 1993). The asymmetric unit of compound (I) is shown in Fig. 1, while the two molecules, *A* and *B*, of compound (II) are shown in Fig. 2. In compound (II), one C atom in molecule *B* (C14*B*) is disordered and was included in the least-squares anisotropic refinement of the structure as C14*B*1 [occupancy 0.47 (2)] and C14*B*2 [occupancy 0.53 (2)]. H atoms on C13, C14 and C15 were included unrefined in the final least-squares refinement, with partial occupancies. The dihedral angle between the least-squares planes of the benzene and pyrone rings in both compounds are normal. Values for the torsion angles C8—C7—N16—C15 [177.6 (2) in (I), and −178.3 (4) for molecule *A* and −175.9 (4)° for molecule *B* in (II)] and C6—C7—N16—C15 [−1.3 (3) in

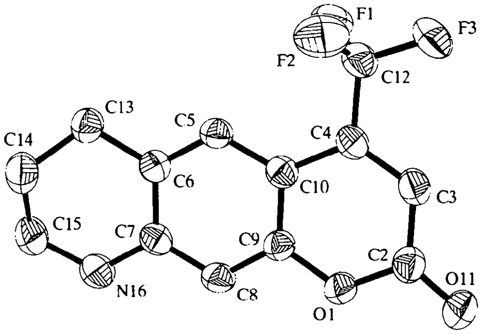


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I) showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

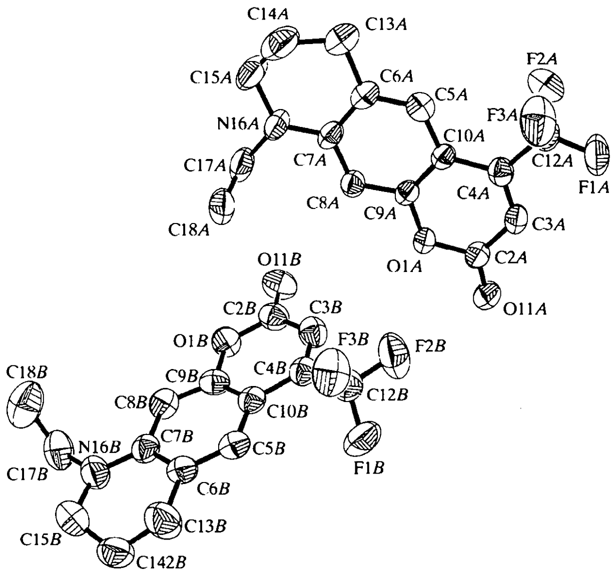


Fig. 2. *ORTEP*II (Johnson, 1976) drawing of (II) showing the atomic numbering schemes of molecules *A* and *B*. Displacement ellipsoids are shown at the 50% probability level.

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(I), and 0.8 (6) for molecule *A* and 4.0 (6)° for molecule *B* in (II)] suggest a sofa conformation for the piperazine ring similar to that observed in coumarin 339 (Jasinski & Woudenberg, 1993), which has values of −178.3 (3) and 3.3 (4)°, respectively.

Molecules in compound (I) are stacked along the *a* axis with an interlayer spacing of 3.485 (2) Å (Fig. 3). In (II), molecules are stacked in layers in an [+*A*][−*B*] repeat pattern midway between the *a* and *c* axes with an [+*A*][−*B*] interlayer spacing of 3.439 (6) Å (Fig. 4). Both these values are less than that observed in coumarin 339 [3.684 (6) Å; Jasinski & Woudenberg, 1993]. Substitution of a more bulky trifluoromethyl group in place of a methyl group at C4 to give coumarin 340, (I), and further addition of an ethyl group at N16 of the piperazine ring to give coumarin 355, (II), may indicate a structural significance that is related to the slightly different luminescent and laser-dye characteristics of these three similar compounds.

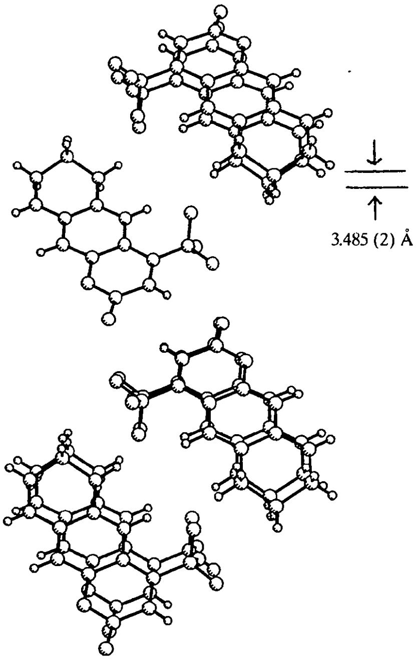

Fig. 3. *PLUTO* (Motherwell & Clegg, 1978) drawing of the stacking arrangement of the molecules in (I) viewed along the *a* axis.

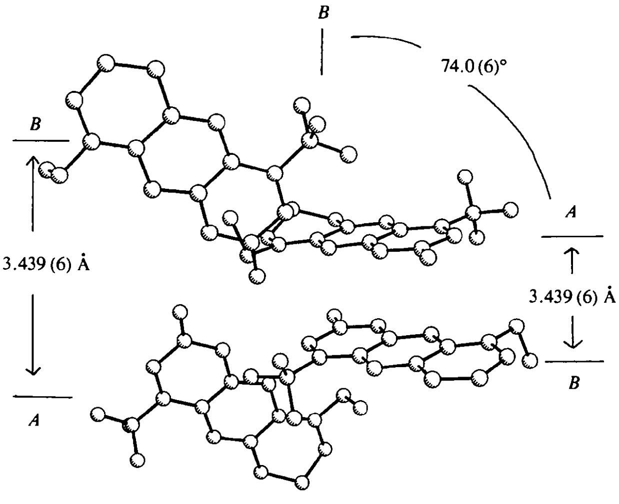

Fig. 4. *PLUTO* (Motherwell & Clegg, 1978) drawing of the stacking arrangement of the molecules in (II) viewed midway between the *a* and *c* axes.

Experimental

Compounds (I) and (II) were obtained from Kodak and Exiton, respectively. Each was recrystallized from acrylonitrile by slow evaporation.

Compound (I)

Crystal data

$C_{13}H_{10}F_3NO_2$
M_r = 269.2
Triclinic
$P\bar{1}$
a = 11.044 (2) Å
b = 11.809 (2) Å
c = 4.6958 (7) Å
α = 92.74 (1)°
β = 95.04 (1)°
γ = 111.337 (10)°
V = 566.1 (2) Å^3
Z = 2
D_x = 1.579 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 24 reflections
θ = 41.05–47.47°
μ = 0.1321 mm^{-1}
T = 296 K
Needle
1.0 × 0.5 × 0.2 mm
Yellow

Data collection

Rigaku AFC-6*S* diffractometer
ω scans with profile analysis
Absorption correction:
ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.980, $T_{\max}$ = 1.000
2114 measured reflections
2001 independent reflections

1386 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.037
$\theta_{\max}$ = 25.0°
$h = 0 \rightarrow 13$
$k = -14 \rightarrow 13$
$l = -5 \rightarrow 5$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.036
$wR(F^2)$ = 0.092
S = 1.09
2001 reflections
213 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.0471P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.003
$\Delta\rho_{\max}$ = 0.15 e Å^{-3}
$\Delta\rho_{\min}$ = −0.16 e Å^{-3}
Extinction correction: *SHELXL93*
Extinction coefficient: 0.049 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*—H···*A*
N16—H16···O11^{i}	0.92 (3)	2.25 (3)	166 (2)
C3—H3···O11^{ii}	0.90 (2)	2.69 (2)	176 (2)
C8—H8···O1^{i}	0.95 (2)	2.51 (2)	161 (2)
C15—H15*A*···F3^{iii}	0.91 (3)	2.53 (3)	138 (2)

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, -y, 2-z$; (iii) $x-1, y, z-1$.

Compound (II)

Crystal data

$C_{15}H_{14}F_3NO_2$
$M_r = 297.3$
Monoclinic
$P2_1/n$
$a = 9.756\ (4)$ Å
$b = 12.613\ (4)$ Å
$c = 22.443\ (4)$ Å
$\beta = 92.45\ (2)^\circ$
$V = 2759.1\ (15)$ Å^3
$Z = 8$
$D_x = 1.431$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 36.79–42.39^\circ$
$\mu = 0.1154$ mm^{-1}
$T = 296$ K
Prism
0.6 × 0.5 × 0.3 mm
Yellow

Data collection

Rigaku AFC-6*S* diffractometer
ω scans with profile analysis
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.938$, $T_{\max} = 1.000$
5158 measured reflections
4856 independent reflections

2236 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 25.0^\circ$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 15$
$l = -26 \rightarrow 26$
3 standard reflections every 150 reflections intensity decay: 0.41%

Refinement

Refinement on F^2
$R(F) = 0.055$
$wR(F^2) = 0.127$
$S = 1.17$
4850 reflections
389 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 1.0311P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1988); program(s) used to solve structures: *MITHRIL* (Gilmore, 1984); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *TEXSAN GRAPHICS*; software used to prepare material for publication: *TEXSAN FINISH*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1297). Services for accessing these data are described at the back of the journal.

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1,4-Bis(triphenylmethoxy)-2-butyne, Rhombohedral with $Z' = \frac{7}{6}$

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Abstract

The title compound, $C_{42}H_{34}O_2$, crystallizes in the space group $R\bar{3}$ with one molecule disordered at a crystallographic $\bar{3}$ site and another in a general position. The conformation of the linkage of the trityl groups to the central butyne group is such that the O—C···C—O grouping forms a torsion angle of magnitude 87.2 (2)°. The C≡C length in the ordered molecule is 1.176 (3) Å.

Comment

The ditritylated title compound, (1), was isolated as a minor side-product during the synthesis of 4-tri-

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