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7-Amino-4-methylcoumarin

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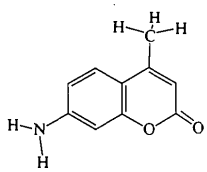
Abstract

In the title compound, $C_{10}H_9NO_2$, the dihedral angle between the least-squares planes of the benzene (C5—C6—C7—C8—C9—C10) and pyrone (O1—C2—C3—C4—C10—C9) rings is 1.49 (3)°. The crystal structure is stabilized by three intermolecular hydrogen-bonded contacts involving C—H···O [3.389 (2) Å] and N—H···O [2.982 (2) and 3.168 (3) Å] interactions.

Comment

The title compound, (I), an aminocoumarin laser dye also known as coumarin 120 (Eastman Kodak Co., Rochester, NY, USA) or coumarin 440 (Exiton Inc., Dayton, Ohio, USA), has been observed to produce laser emissions in the 370–760 nm region, pumped by an XeF eximer laser (Eschrich & Morgan, 1985), and in the visible region by various other continuous wave (CW) lasers (Tuccio, Drexhage & Reynolds, 1973; Yarborough, 1974; Kato, 1975). Structural details of several related aminocoumarin laser-dye compounds have been reported (Selladurai & Subramanian, 1992; Chinnakali, Sivakumar & Natarajan, 1989, 1990; Chinnakali, Sivakumar, Natarajan & Mathews, 1992; Chinnakali, Selladurai, Sivakumar, Subramanian & Natarajan, 1990; Masilamani, Chandrasekar, Sivaram, Sivasankar & Natarajan, 1986; Messager & Delugeard, 1974; Murthy, Ramamurthy & Venkatesan, 1988).



(I)

An *ORTEP* view (Johnson, 1976) of the title compound with atomic labeling is shown in Fig. 1. Bond lengths and angles in the coumarin moiety are normal (Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985). The dihedral angle between the least-squares planes of the slightly distorted pyrone [χ^2 = 153.2] and planar benzene [χ^2 = 18.5] rings is 1.49 (3)°. The torsion angles O11—C2—O1—C9 [−177.9 (2)°] and O11—C2—C3—C4 [178.6 (2)°] indicate a slight deviation from planarity in the pyrone ring resulting from a minor displacement of the atom C2 from the least-squares plane calculated from the positions of the remaining atoms in the ring.

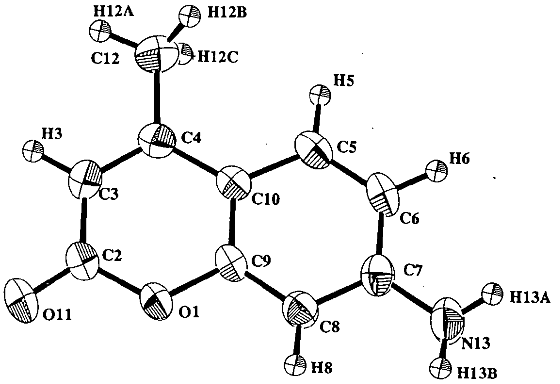


Fig. 1. *ORTEP* (Johnson, 1976) drawing (50% probability ellipsoids) and atomic numbering scheme.

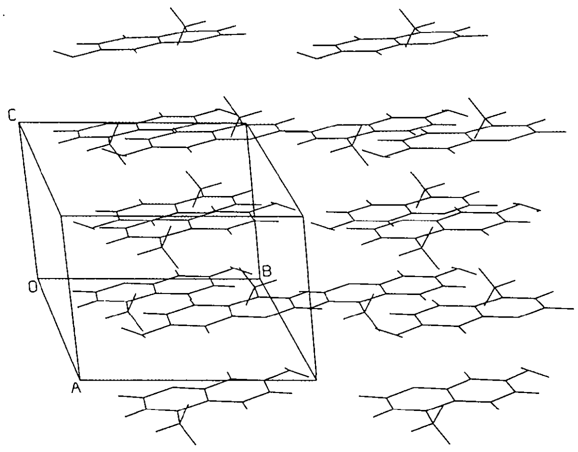


Fig. 2. Molecular packing of the title compound in the unit cell viewed down the *a* axis.

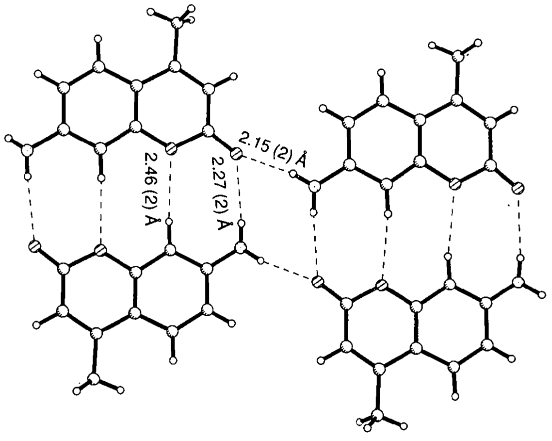


Fig. 3. Hydrogen bonding of the title compound in the *ab* plane (distances in Å).

The packing of the molecules in the unit cell viewed down the *a* axis is shown in Fig. 2. The molecules are linked by one hydrogen bond of the C—H$\cdots$O type [C8$\cdots$O1^{i} 3.389 (2), C8—H8 0.97 (2), H8$\cdots$O1^{i} 2.46 (2) Å and C8—H8$\cdots$O1^{i} 160.5 (7)°; symmetry code: (i) $-x$, $1-y$, $-z$] and two hydrogen bonds of the N—H$\cdots$O type [N13$\cdots$O11^{ii} 2.989 (2), N13—H13*A* 0.85 (2), H13*A*$\cdots$O11^{ii} 2.15 (2) Å and N13—H13*A*$\cdots$O11^{ii} 172.8 (7)°; N13$\cdots$O11^{i} 3.168 (3), N13$\cdots$H13*B* 0.90 (2), H13*B*$\cdots$O11^{i} 2.27 (2) Å and N13—H13*B*$\cdots$O11^{i} 174.8 (6)°; symmetry code: (ii) x, $1+y$, z] (Taylor & Kennard, 1982) as shown in Fig. 3.

Experimental

Prismatic crystals of the title compound (Exiton Chemical Company, Dayton, Ohio 45431, USA) were grown from acetonitrile by slow evaporation.

Crystal data

$C_{10}H_9NO_2$
$M_r = 175.19$
Triclinic
$P\bar{1}$
$a = 7.157$ (1) Å
$b = 9.566$ (1) Å
$c = 6.920$ (1) Å
$\alpha = 95.13$ (1)°
$\beta = 110.11$ (1)°
$\gamma = 71.78$ (1)°
$V = 422.5$ (2) Å^3
$Z = 2$
$D_x = 1.377$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 22.1$–$24.9°$
$\mu = 0.0907$ mm^{-1}
$T = 296$ K
Prism
0.90 × 0.40 × 0.20 mm
Colorless

Data collection

Rigaku AFC-6*S* diffractometer
ω scans with profile analysis
Absorption correction: empirical (ψ scan)
$T_{\min} = 0.92$, $T_{\max} = 0.98$
2089 measured reflections
1934 independent reflections
1232 observed reflections [$I > 3.0\sigma(I)$]

$R_{\rm int} = 0.012$
$\theta_{\max} = 27.50°$
$h = 0 \rightarrow 9$
$k = -11 \rightarrow 12$
$l = -8 \rightarrow 8$
3 standard reflections monitored every 150 reflections intensity variation: 2.20%

Refinement

Refinement on *F*
$R = 0.041$
$wR = 0.050$
$S = 1.901$
1232 reflections
155 parameters
All H-atom parameters refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.0056$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Extinction correction: Type 2 Gaussian isotropic (Zachariasen, 1963)
Extinction coefficient: 2.8325×10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.2784 (2)	0.3406 (1)	0.1452 (2)	0.0421
O11	0.3033 (2)	0.1066 (1)	0.1105 (3)	0.0632
N13	0.1645 (3)	0.8550 (2)	0.1726 (3)	0.0527
C2	0.3994 (3)	0.1963 (2)	0.1655 (3)	0.0430
C3	0.6198 (3)	0.1672 (2)	0.2488 (3)	0.0431
C4	0.7113 (3)	0.2754 (2)	0.3013 (3)	0.0368
C5	0.6519 (3)	0.5510 (2)	0.3143 (3)	0.0412
C6	0.5175 (3)	0.6906 (2)	0.2808 (3)	0.0424
C7	0.3005 (3)	0.7152 (2)	0.2026 (3)	0.0379
C8	0.2260 (3)	0.5940 (2)	0.1614 (3)	0.0380
C9	0.3654 (3)	0.4548 (2)	0.1951 (3)	0.0339
C10	0.5812 (3)	0.4263 (2)	0.2727 (3)	0.0338
C12	0.9434 (3)	0.2396 (3)	0.3883 (4)	0.0517

Table 2. *Selected geometric parameters* (Å, °)

O1—C2	1.371 (2)	C4—C12	1.495 (2)
O1—C9	1.382 (2)	C5—C6	1.365 (2)
O11—C2	1.218 (2)	C5—C10	1.406 (2)
N13—C7	1.369 (2)	C6—C7	1.406 (2)
C2—C3	1.424 (3)	C7—C8	1.391 (2)
C3—C4	1.351 (2)	C8—C9	1.374 (2)
C4—C10	1.440 (2)	C9—C10	1.393 (2)
C2—O1—C9	121.8 (1)	N13—C7—C6	121.1 (2)
O1—C2—O11	115.2 (2)	N13—C7—C8	120.4 (2)
O1—C2—C3	117.5 (1)	C6—C7—C8	118.5 (2)
O11—C2—C3	127.3 (2)	C7—C8—C9	119.4 (2)
C2—C3—C4	122.6 (2)	O1—C9—C8	115.6 (1)
C3—C4—C10	118.9 (2)	O1—C9—C10	120.7 (1)
C3—C4—C12	120.7 (2)	C8—C9—C10	123.7 (2)
C10—C4—C12	120.4 (2)	C4—C10—C5	125.8 (2)
C6—C5—C10	122.0 (2)	C4—C10—C9	118.5 (1)
C5—C6—C7	120.8 (2)		

Weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of two rescans) and the counts accumulated to assure good counting satistics. Lp corrections were applied; no correction was made for decay. Plots of $\Sigma w(|F_o|-|F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. In the weighting scheme, $\sigma^2(F_o^2) = [S^2(C + 4B) + (0.03F_o^2)]/{\rm Lp}^2$, where S is the scan rate, C is the number of counts per scan and B is the sum of two background counts.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HH1048). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-Methylthiocarbamoyltetrathiafulvalene at 150 K

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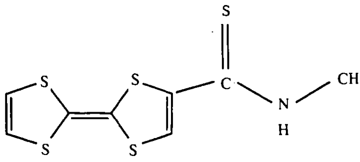
Abstract

The crystal structure of the title compound, 4-(*N*-methylthiocarbamoyl)-2,2′-bi(1,3-dithiolylidene), C_8H_7-NS_5, has been re-determined at 150 K and is compared with that determined by an ambient-temperature study, showing essentially the same motif (κ packing of dimers) and strongly anisotropic thermal expansion.

Comment

Recently we studied the crystal structure of *N*-methylthiocarbamoyltetrathiafulvalene, (1), at ambient temperature (Batsanov, Bryce, Cooke, Heaton & Howard, 1993; Batsanov *et al.*, 1994), which provided the first example of κ-phase packing of neutral TTF (TTF = tetrathiafulvalene) donor molecules. Herein we report the re-investigation of the structure of (1) at 150 K.



(1)

The structure is essentially the same as at 293 K. Parallel (inversionally equivalent) molecules form dimers with close contacts between the central, almost planar C_2S_4 moieties. The interplanar separation between the molecules [3.32 (5) Å] is slightly shorter than at 293 K [3.41 (4) Å], as is the shortest C(4)···C(4′) distance [3.338 (5) *versus* 3.401 (7) Å]. The peripheral C=C moieties of the TTF molecules are bent outwards from the dimer slightly more than at 293 K. The substituted and unsubstituted rings are folded along the S···S vectors with angles of 23.6 (1) and 14.5 (1)°, compared with 22.8 (1) and 13.9 (1)°, respectively, at 293 K.

The dimers are packed in a κ fashion, *i.e.* with the longest axes of the molecules parallel and their

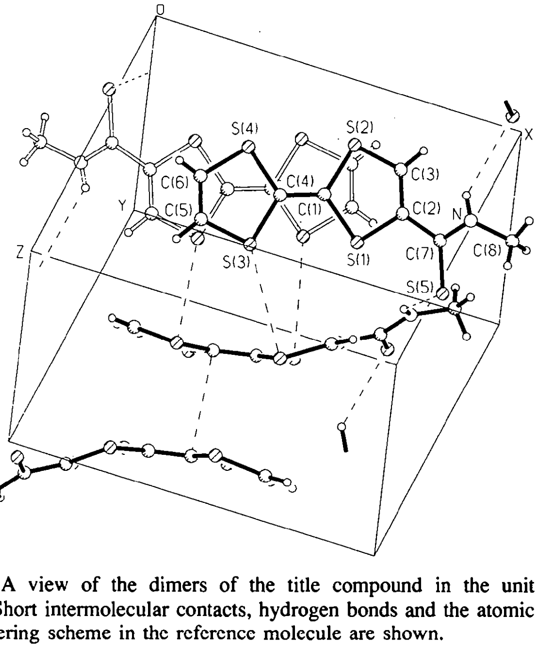


Fig. 1. A view of the dimers of the title compound in the unit cell. Short intermolecular contacts, hydrogen bonds and the atomic numbering scheme in the reference molecule are shown.

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