

Acta Cryst. (1995). **C51**, 2585–2586

4-(4-Chloroanilinomethyl)-6-methylcoumarin

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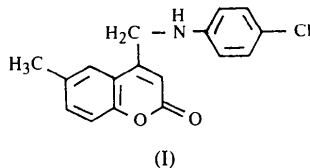
(Received 19 July 1994; accepted 11 May 1995)

Abstract

The structure of the title compound, $C_{17}H_{14}ClNO_2$, is reported. The benzene ring of the 1-benzopyran-2(1*H*)-one (coumarin) moiety makes a dihedral angle of $1.01(13)^\circ$ with the pyrone ring and the benzene ring of the *p*-chloroanilinomethyl moiety makes a dihedral angle of $101.62(10)^\circ$ with the mean plane of the coumarin moiety. The molecules are held together by $N-H\cdots O$ hydrogen bonds.

Comment

The title compound, (I), is one of a series of 4-anilino-methylcoumarins (Kulkarni & Patil, 1981) reported as possible antibacterial agents. Various substituents at atom C(4) play a vital role in structure–activity studies of the induction of drug metabolizing enzymes by coumarins (Wald & Feuer, 1971). The tunability of the coumarin system in the field of laser dyes (Dienes, Shank & Trozzolo, 1970) is of interest. The present work is a continuation of structure analyses of coumarin derivatives.



An *ORTEP* (Johnson, 1965) plot of (I) is shown in Fig. 1. The structure consists of a 6-methylcoumarin moiety connected to a *p*-chloroanilinomethyl moiety. The benzene and pyrone rings of the coumarin moiety are planar and form a dihedral angle of $1.10(13)^\circ$. The benzene ring of the *p*-chloroanilino group is planar

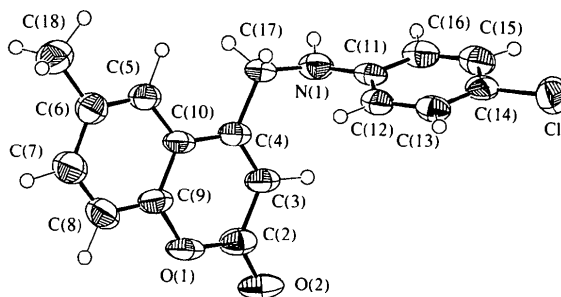


Fig. 1. An *ORTEP* (Johnson, 1965) plot of the title compound with 50% probability displacement ellipsoids.

and makes a dihedral angle of $101.62(10)^\circ$ with the coumarin moiety.

The bonds $C(2)-O(2)$ [$1.208(4)\text{ \AA}$] and $C(3)-C(4)$ [$1.341(5)\text{ \AA}$] of the pyrone ring are shorter than expected and show distinct double-bond character (Shimizu, Kashino & Haisa, 1975). The $C_{sp^2}(11)-N(1)$ bond [$1.383(4)\text{ \AA}$] is, as expected, shorter than $C_{sp^3}(17)-N(1)$ [$1.454(5)\text{ \AA}$], as a result of the delocalization of the N-atom lone pair with the π electrons of the benzene ring. This is also reflected in the enhanced $C(14)-Cl$ bond distance of $1.748(3)\text{ \AA}$, as observed in the crystal structure of *p*-chloroaniline (Trotter, Whitlow & Zobel, 1966), where the observed $C_{sp^2}-N$ and $C_{sp^2}-Cl$ bond lengths are 1.39 and 1.75 \AA , respectively.

The torsion angle $C(4)-C(17)-N(1)-C(11)$ of $-89.9(3)^\circ$ shows a *gauche* relationship between the 6-methylcoumarin moiety and the *p*-chloroanilino moiety about the $C(17)-N(1)$ bond. The torsion angle $O(2)-C(2)-C(3)-C(4)$ of $-178.2(5)^\circ$ shows that the carbonyl O atom and the *p*-chloroanilino group are mutually *anti* about the $C(2)-C(3)$ bond.

From Fig. 2 it can be seen that the molecules are held together in pairs by intermolecular hydrogen bonds between $N-H$ groups and the carbonyl O atoms, with a $H\cdots O$ distances of $2.09(4)\text{ \AA}$; all other contacts are of the van der Waals type.

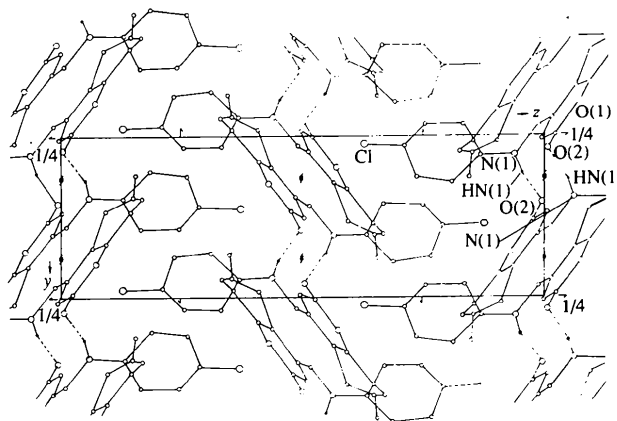


Fig. 2. The molecular packing viewed down the *a* axis.

Experimental

Single crystals of the title compound were supplied by Dr M. V. Kulkarni, Department of Chemistry, Karnatak University, Dharwad, India.

Crystal data

C₁₇H₁₄ClNO₂ $M_r = 299.77$

Orthorhombic

 $P2_12_12_1$ $a = 14.040(3) \text{ \AA}$ $b = 5.804(1) \text{ \AA}$ $c = 17.728(2) \text{ \AA}$ $V = 1444.7(4) \text{ \AA}^3$ $Z = 4$ $D_x = 1.378 \text{ Mg m}^{-3}$ $D_m = 1.37 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation $\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25

reflections

 $\theta = 20\text{--}25^\circ$ $\mu = 0.26 \text{ mm}^{-1}$ $T = 300 \text{ K}$

Plate

 $0.3 \times 0.2 \times 0.2 \text{ mm}$

Light brown

Data collection

Enraf-Nonius CAD-4

diffractometer

 ω - 2θ scans

Absorption correction:

none

2903 measured reflections

2530 independent reflections

2218 observed reflections

 $[I > 2.5\sigma(I)]$ $R_{\text{int}} = 0.0197$ $\theta_{\text{max}} = 25^\circ$ $h = -13 \rightarrow 16$ $k = 0 \rightarrow 6$ $l = -21 \rightarrow 21$

3 standard reflections

monitored every 167

reflections

intensity decay: 2–3%

Refinement

Refinement on F $R = 0.041$ $wR = 0.033$ $S = 4.41$

2218 reflections

246 parameters

All H-atom parameters

refined

 $w = 1/\sigma^2(F)$ $(\Delta/\sigma)_{\text{max}} = 0.623$ $\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$

Atomic scattering factors

from Cromer & Mann

(1968) and Stewart,

Davidson & Simpson

(1965)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

| | x | y | z | B_{eq} |
|-------|------------|-------------|-------------|-----------------|
| Cl | 0.8869 (1) | 0.0420 (2) | 0.3915 (1) | 5.71 (5) |
| O(1) | 1.1384 (1) | -0.2085 (5) | -0.0710 (1) | 4.60 (12) |
| O(2) | 1.1958 (1) | 0.0775 (5) | -0.0025 (1) | 6.01 (14) |
| C(2) | 1.1260 (2) | -0.0289 (7) | -0.0216 (2) | 4.32 (17) |
| C(3) | 1.0286 (2) | 0.0224 (7) | 0.0042 (2) | 4.04 (17) |
| C(4) | 0.9555 (2) | -0.1094 (6) | -0.0185 (2) | 3.58 (16) |
| C(5) | 0.8984 (2) | -0.4435 (7) | -0.0996 (2) | 4.03 (16) |
| C(6) | 0.9175 (2) | -0.6181 (7) | -0.1496 (2) | 4.32 (17) |
| C(7) | 1.0125 (2) | -0.6596 (7) | -0.1723 (2) | 4.83 (19) |
| C(8) | 1.0841 (2) | -0.5220 (7) | -0.1443 (2) | 4.69 (18) |
| C(9) | 1.0635 (2) | -0.3444 (7) | -0.0954 (2) | 4.03 (17) |
| C(10) | 0.9698 (2) | -0.2978 (6) | -0.0703 (2) | 3.52 (16) |
| C(11) | 0.8575 (2) | 0.1055 (6) | 0.1385 (2) | 3.57 (16) |
| C(12) | 0.9012 (2) | -0.0879 (6) | 0.1710 (2) | 3.73 (16) |
| C(13) | 0.9106 (2) | -0.1054 (6) | 0.2487 (2) | 3.77 (16) |
| C(14) | 0.8766 (2) | 0.0668 (7) | 0.2936 (2) | 3.96 (17) |
| C(15) | 0.8342 (2) | 0.2613 (7) | 0.2633 (2) | 4.58 (18) |
| C(16) | 0.8252 (2) | 0.2800 (7) | 0.1856 (2) | 4.32 (18) |

| | | | | |
|-------|------------|-------------|-------------|-----------|
| N(1) | 0.8466 (2) | 0.1300 (6) | 0.0614 (1) | 4.44 (15) |
| C(17) | 0.8543 (2) | -0.0657 (7) | 0.0106 (2) | 4.33 (17) |
| C(18) | 0.8378 (3) | -0.7695 (8) | -0.1813 (2) | 5.45 (21) |

Table 2. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|------------------|-----------|-------------------|-----------|
| O(1)—C(2) | 1.372 (4) | C(5)—C(10) | 1.410 (5) |
| O(2)—C(2) | 1.208 (4) | C(4)—C(17) | 1.533 (4) |
| C(2)—C(3) | 1.472 (4) | C(17)—N(1) | 1.454 (5) |
| C(3)—C(4) | 1.341 (5) | N(1)—C(11) | 1.383 (4) |
| C(4)—C(10) | 1.443 (5) | C(11)—C(12) | 1.403 (5) |
| C(10)—C(9) | 1.415 (4) | C(12)—C(13) | 1.388 (4) |
| C(9)—O(1) | 1.384 (4) | C(13)—C(14) | 1.364 (5) |
| C(9)—C(8) | 1.377 (5) | C(14)—C(15) | 1.384 (5) |
| C(8)—C(7) | 1.376 (5) | C(15)—C(16) | 1.388 (5) |
| C(7)—C(6) | 1.414 (5) | C(16)—C(11) | 1.389 (5) |
| C(6)—C(18) | 1.529 (5) | C(14)—Cl | 1.748 (3) |
| C(6)—C(5) | 1.373 (5) | | |
| C(9)—O(1)—C(2) | 122.4 (2) | C(7)—C(6)—C(5) | 119.6 (3) |
| O(1)—C(2)—O(2) | 117.7 (3) | C(18)—C(6)—C(5) | 121.2 (3) |
| O(1)—C(2)—C(3) | 118.0 (3) | C(6)—C(5)—C(10) | 122.7 (3) |
| O(2)—C(2)—C(3) | 124.3 (3) | C(4)—C(17)—N(1) | 114.0 (3) |
| C(2)—C(3)—C(4) | 120.1 (3) | C(17)—N(1)—C(11) | 121.6 (3) |
| C(3)—C(4)—C(10) | 121.1 (3) | N(1)—C(11)—C(12) | 122.4 (3) |
| C(3)—C(4)—C(17) | 121.0 (3) | N(1)—C(11)—C(16) | 118.9 (3) |
| C(10)—C(4)—C(17) | 117.9 (3) | C(16)—C(11)—C(12) | 118.7 (3) |
| C(4)—C(10)—C(9) | 118.3 (3) | C(11)—C(12)—C(13) | 120.5 (3) |
| C(4)—C(10)—C(5) | 126.1 (3) | C(12)—C(13)—C(14) | 119.5 (3) |
| C(5)—C(10)—C(9) | 115.6 (3) | C(13)—C(14)—C(15) | 121.5 (3) |
| C(10)—C(9)—O(1) | 119.9 (3) | C(14)—C(15)—C(16) | 119.2 (3) |
| C(8)—C(9)—O(1) | 117.7 (3) | C(15)—C(16)—C(11) | 120.7 (3) |
| C(10)—C(9)—C(8) | 122.4 (3) | C(13)—C(14)—Cl | 119.3 (3) |
| C(9)—C(8)—C(7) | 120.5 (3) | C(15)—C(14)—Cl | 119.2 (3) |
| C(8)—C(7)—C(6) | 119.2 (3) | | |

The atomic coordinates of the non-H atoms were determined by direct methods using *SHELXS86* (Sheldrick, 1985) and refined along with anisotropic displacement parameters. All H atoms were located from a difference Fourier map and refined with isotropic displacement parameters using the *NRCVAX* structure solution program (Larson, Lee, Le Page, Webster, Charland, Gabe & White, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1165). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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