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Crystal structure of 8-methoxy-3-dibromoacetylcoumarin, $C_{12}H_8Br_2O_4$

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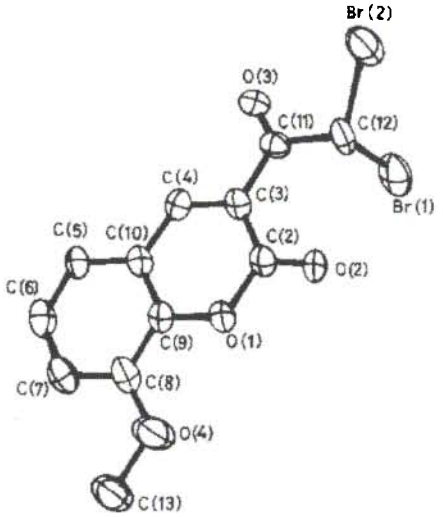

Abstract

$C_{12}H_8Br_2O_4$, monoclinic, $P12_1/c1$ (No. 14), $a = 11.546(2)$ Å, $b = 6.885(4)$ Å, $c = 15.949(3)$ Å, $\beta = 101.75(2)°$, $V = 1241.3$ Å^3, $Z = 4$, $\rho_m = 2.040$ g·cm^{-3}, $R_{all}(F) = 0.039$, $wR_{all}(F) = 0.043$, $T = 300$ K.

Source of material

Synthesis of the title compound follows the bromination of 3-acetyl-coumarin in presence of $CHCl_3$ [1].

Discussion

The coumarin moiety with various groups at position 3 has given rise to many derivatives of biological and structural importance. 3-bromoacetylcoumarin [1] is a key intermediate in the synthesis of some 3-heterocyclic coumarins [2] and many other compounds of biological relevance [3]. A preliminary examination of its structure shows that due to free rotation about the C(3)—CO bond this molecule can have two conformations. In these two conformers the carbonyl group attached to C(3) can be *S-cis*(I) or *S-trans*(II) to C(3)—C(4) double bond of the pyrone ring. Further, many O-haloketones are known to exhibit interesting conformations [4] which have been explained using different projection formulae. To establish the preferred conformation of the title compound in the solid state, the structure analysis has been carried out.

The coumarin moiety is planar and makes a dihedral angle of 5.3(5)° with planar carbonyl group attached to C(3). The molecules are packed in parallel layers. The coumarin moiety possesses a highly planar phenyl ring compared to pyrone ring which makes a dihedral angle of 1.2(2)° with the mean plane of the pyrone ring. The torsion angles O(3)–C(11)–C(12)–Br(1) = –92.0(6)° and O(3)–C(11)–C(12)–Br(2) = –152.3(4)° indicate that the molecule does not have an eclipsed conformation in solid state as observed in the case of 3-bromoacetyl-coumarin [5]. The torsion angle C(4)–C(3)–C(11) = –4.5(8)° indicates the C(3) carbonyl oxygen O(3) is *cis* to C(4) about C(3)—C(11) bond. This allows maximum seperation of O(2) and O(3) which is reflected in the increased bond angle O(2)–C(2)–C(3) = 127.4(5)° but the angle C(3)–C(11)–C(12) = 119.1(5)° is small compared to that observed 3-acetyl-6-bromocoumarin [6] and this may be due to the heavy atoms Br(1) and Br(2) attached to C(12). The bond lengths and angles in the coumarin moiety agree with the values observed in 3-bromoacetylcoumarin [5] with in the experimental errors. As usual the bond lengths and angles in the benzene ring shows variations due to fusion of the pyrone ring [6] and have an average value 1.392(9) Å and 120.0° respectively. The C(3)—C(4) and C(2)—O(2) bonds are shorter than the expected values and are distinctly double bond in character. The angle O(2)–C(2)–C(1) is generally smaller than the angle O(2)–C(2)–C(3) because of steric effect of the substituent at C(3). The bond distances of the terminal bromine atoms C(12)—Br(1) = 1.945(6) Å and C(12)—Br(2) = 1.920(6) Å are longer than the values observed in many coumarins containing bromines attached to phenyl ring. But angles around C(12) are almost comparable to normal tetrahedral angle. The bond length C(11)—O(3) = 1.195(8) Å is almost close to the normal bond length 1.22 Å. The bond length C(2)—C(3) = 1.454(8) Å is shorter than the normal C_{sp2}-C_{sp2} bond distance 1.487 Å might due to the σ-electron delocalization and electrostatic effect.

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.25 × 0.5 × 1.0 mm
Wavelength:	Mo K_α radiation (0.70930 Å)
μ:	32.8 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, ω/2θ
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2504, 2176
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 6\ \sigma(I_{obs})$, 1465
$N(param)_{refined}$:	163
Programs:	SHELXS-86 [7], SHELX-76 [8], ORTEP [9]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(4)	4*e*	0.960(5)	0.339(8)	0.978(3)	0.1860(2)
H(5)	4*e*	1.038(5)	0.131(8)	1.083(3)	0.1610(2)
H(6)	4*e*	1.176(7)	0.11(1)	1.190(4)	0.1130(3)
H(7)	4*e*	1.320(5)	0.179(8)	1.122(4)	0.0530(2)
H(12)	4*e*	0.768(7)	0.52(1)	0.730(4)	0.0670(2)
H(13A)	4*e*	1.459(6)	0.28(1)	0.953(4)	0.0720(2)
H(13B)	4*e*	1.445(6)	0.15(1)	1.018(4)	0.0880(2)
H(13C)	4*e*	1.466(7)	0.35(1)	1.062(5)	0.1840(3)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	4*e*	0.7117(1)	0.1993(1)	0.6646	0.0536(4)	0.0816(6)	0.0544(4)	–0.0039(4)	–0.0014(3)	–0.0264(4)
Br(2)	4*e*	0.5645(1)	0.5649(1)	0.7119	0.0448(4)	0.0798(5)	0.0591(4)	0.0177(4)	–0.0015(3)	0.0014(4)
O(1)	4*e*	1.0792(3)	0.3340(6)	0.8771(2)	0.035(2)	0.054(2)	0.027(2)	0.004(2)	0.003(2)	0.001(2)
O(2)	4*e*	0.9637(3)	0.4357(6)	0.7585(2)	0.045(2)	0.072(3)	0.023(2)	0.001(2)	0.004(2)	0.004(2)
C(2)	4*e*	0.9677(5)	0.3743(8)	0.8300(3)	0.033(3)	0.038(3)	0.033(3)	0.000(3)	0.003(2)	–0.009(3)
C(3)	4*e*	0.8686(5)	0.3358(8)	0.8771(3)	0.036(3)	0.031(3)	0.033(3)	–0.001(3)	0.003(2)	–0.008(2)
C(4)	4*e*	0.8892(5)	0.2790(7)	0.9552(3)	0.047(3)	0.029(3)	0.035(3)	–0.008(3)	0.008(3)	–0.006(2)
C(5)	4*e*	1.0296(6)	0.1955(8)	1.0910(3)	0.061(4)	0.031(3)	0.033(3)	0.001(3)	0.000(3)	–0.005(3)
C(6)	4*e*	1.1438(6)	0.1676(8)	1.1311(3)	0.065(4)	0.032(3)	0.032(3)	0.005(3)	–0.002(3)	–0.000(3)
C(7)	4*e*	1.2376(6)	0.1917(9)	1.0891(4)	0.051(4)	0.047(4)	0.043(3)	0.013(3)	0.007(3)	–0.004(3)
C(8)	4*e*	1.2156(5)	0.2499(8)	1.0029(4)	0.042(3)	0.041(3)	0.037(3)	0.005(3)	0.004(3)	–0.008(3)
C(9)	4*e*	1.1003(5)	0.2780(8)	0.9617(3)	0.045(3)	0.037(3)	0.028(3)	0.002(3)	0.005(3)	–0.005(2)
C(10)	4*e*	1.0062(5)	0.2527(7)	1.0024(3)	0.043(3)	0.003(3)	0.027(3)	–0.001(3)	0.001(2)	–0.002(2)
C(11)	4*e*	0.7424(5)	0.3596(8)	0.8277(3)	0.032(3)	0.045(3)	0.040(3)	–0.001(3)	0.004(3)	–0.003(3)
C(12)	4*e*	0.7134(5)	0.4309(9)	0.7352(3)	0.038(3)	0.058(4)	0.034(3)	0.006(3)	0.001(2)	–0.006(3)
O(3)	4*e*	0.6653(4)	0.3183(7)	0.8644(3)	0.035(2)	0.098(4)	0.052(3)	–0.009(3)	0.005(2)	0.012(3)
O(4)	4*e*	1.2998(4)	0.2835(7)	0.9562(3)	0.037(2)	0.089(4)	0.052(3)	0.010(7)	0.001(2)	–0.001(2)
C(13)	4*e*	1.4194(6)	0.2696(1)	0.9992(5)	0.038(4)	0.130(8)	0.063(4)	0.014(4)	–0.007(3)	–0.012(4)

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