Crystal structure of dimethyl 6-bromo-2*H*-1-benzopyran-2,3-dicarboxylate, $C_{13}H_{11}BrO_5$

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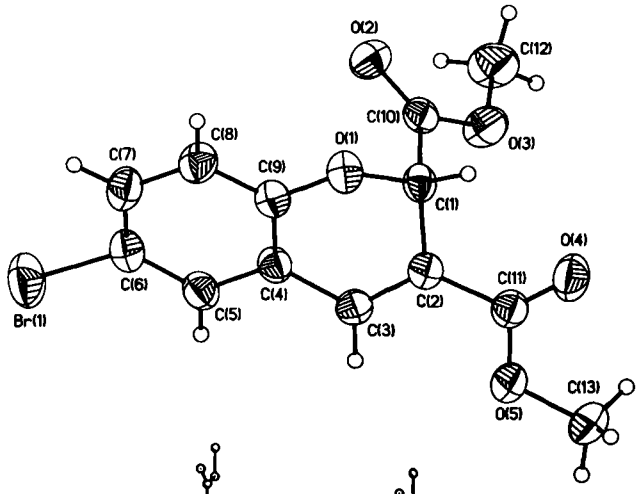

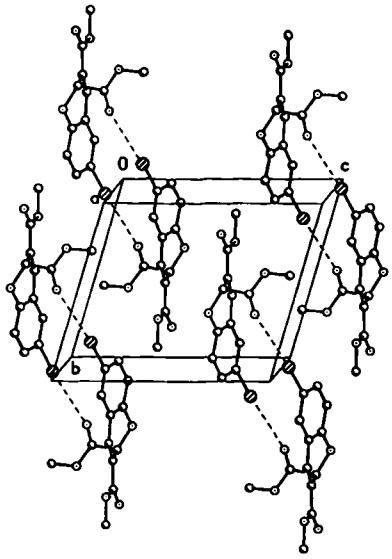

Abstract

$C_{13}H_{11}BrO_5$, triclinic, $P\bar{1}$ (No. 2), $a = 6.2993(7)$ Å, $b = 9.737(1)$ Å, $c = 11.142(1)$ Å, $\alpha = 104.313(3)°$, $\beta = 103.523(3)°$, $\gamma = 92.473(3)°$, $V = 640.1$ Å^3, $Z = 2$, $R_{gt}(F) = 0.036$, $wR_{ref}(F^2) = 0.102$, $T = 293$ K.

Source of material

Dimethyl 6-bromo-2*H*-1-benzopyran-2,3-dicarboxylate was synthesized in accordance with our new procedure [1]. The solution of title compound (0.4 g) in methanol (30 ml) left in room temperature for ten days. The colourless crystals were filtered off, washed with cold methanol (6 ml) and dried in vacuum over P_4O_{10} (mp 412 K; yield 85%). Elemental analyses were consistent with the composition $C_{13}H_{11}BrO_5$ (found: C, 48.25%; H, 3.21%; calc. : C, 48.13%; H, 3.39%).

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyser.

Discussion

2*H*-1-Benzopyran derivatives are important intermediates in the synthesis of many natural products and medicinal agents including some potassium-channel activating drugs [1-7]. A feature common to all these compound is the presence of a strongly electron-withdrawing substituent at 6-position of the 2*H*-1-benzopyran ring [1]. In the recent years, there has been increasing interest in the determination of X-ray crystal structures of biologically active compounds [7-9].

In the structure of title molecule (upper figure), the covalent bonds are found to be normal (relevant bond lengths : *d*(Br1—C6) = 1.899(2) Å, *d*(O1—C9) = 1.379(2) Å, *d*(O1—C1) = 1.430(2) Å, *d*(O2—C10) = 1.198(2) Å, *d*(O3—C10) = 1.330(3) Å, *d*(O3—C12) =1.451(3) Å, *d*(O4—C11) = 1.203(2) Å, *d*(O5—C11) = 1.343(3) Å, *d*(O5—C13) =1.444(3) Å, *d*(C1—C2) = 1.516(3) Å, *d*(C1—C10) = 1.530(3) Å, *d*(C2—C3) = 1.332(3) Å, *d*(C2—C11) = 1.475(3) Å, *d*(C3—C4) = 1.453(3) Å; angles at the O atoms : 114.40(14)° at O1, 115.62(17)° at O3 and 115.67(17)° at O5) and are almost the same as in the previous reports [7-9]. The methyl groups at O3 and O5 are approximately in the planes O3–C10–O2 (∠C12–O3–C10–O2 = 0.3(3)°) and O5–C11–O4 (∠C13–O5–C11–O4 = –0.3(3)°), respectively, that agrees well with a participation of O3 and O5 in the electron donation to the carbonyl groups. The torsion angle ∠C3–C2–C11–O4 = –172.7(2)°, shows clearly that the carbonyl group (C11 to O4) and C=C double bond (C3=C2) share approximately a common plane with *S-trans* conformation, probably is as a result of π-systems conjugations.

Intermolecular ring stacking is observed in the structure, probably it is a result of the presence of parallel aromatic benzene rings in the crystal network (lower figure). Intermolecular electrostatic attractive interactions between Br1 and O2 atoms (*d*(Br1···O2) = 3.249(2) Å) are also observed in the crystal structure. This is probably a result of the presence of electron-poor (O2) and electron-rich (S2) atoms in suitable positions of the crystal network. These intermolecular interactions appear to be plausible factors in the stabilization of the crystal packing.

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Table 1. Data collection and handling.

Crystal:	colourless plate, size 0.1 × 0.4 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	32.24 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	60°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5527, 3666
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2648
$N(param)_{refined}$:	174
Programs:	SHELXTL-97 [10], SADABS [11]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	–0.0339	1.5966	0.3962	0.040
H(3A)	2*i*	0.5022	1.4462	0.3079	0.042
H(5A)	2*i*	0.4523	1.1797	0.1804	0.046
H(7A)	2*i*	–0.0438	0.9283	0.2113	0.055
H(8A)	2*i*	–0.1836	1.1269	0.3170	0.049
H(12A)	2*i*	–0.1527	1.7027	0.0124	0.091
H(12B)	2*i*	–0.3633	1.6407	0.0414	0.091
H(12C)	2*i*	–0.2145	1.5373	–0.0238	0.091
H(13A)	2*i*	0.8090	1.8515	0.4078	0.085
H(13B)	2*i*	0.6728	1.8907	0.5103	0.085
H(13C)	2*i*	0.5815	1.9107	0.3729	0.085

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)	2*i*	0.31293(4)	0.87488(2)	0.08663(3)	0.0766(2)	0.0384(1)	0.0731(2)	0.0160(1)	0.0316(1)	0.0050(1)
O(1)	2*i*	–0.0416(2)	1.3886(1)	0.3678(1)	0.0447(7)	0.0340(7)	0.0387(7)	0.0061(6)	0.0208(6)	0.0116(5)
O(2)	2*i*	–0.2778(2)	1.4142(2)	0.1409(2)	0.0431(8)	0.0434(8)	0.0497(9)	–0.0029(6)	0.0019(7)	0.0094(7)
O(3)	2*i*	–0.0861(2)	1.6216(2)	0.1626(2)	0.0478(8)	0.0497(9)	0.0455(9)	–0.0062(7)	–0.0007(6)	0.0223(7)
O(4)	2*i*	0.2551(3)	1.7935(2)	0.4332(2)	0.0553(9)	0.0349(8)	0.072(1)	0.0020(7)	0.0237(8)	0.0009(7)
O(5)	2*i*	0.5553(2)	1.7089(2)	0.3785(2)	0.0388(8)	0.0334(7)	0.070(1)	–0.0007(6)	0.0131(7)	0.0097(7)
C(1)	2*i*	0.0065(3)	1.5175(2)	0.3352(2)	0.0373(9)	0.0297(8)	0.0349(9)	0.0050(7)	0.0146(7)	0.0078(7)
C(2)	2*i*	0.2491(3)	1.5455(2)	0.3441(2)	0.0359(9)	0.0329(9)	0.0314(9)	0.0027(7)	0.0082(7)	0.0085(7)
C(3)	2*i*	0.3553(3)	1.4333(2)	0.3084(2)	0.0310(9)	0.0354(9)	0.040(1)	0.0021(7)	0.0106(7)	0.0107(8)
C(4)	2*i*	0.2409(3)	1.2904(2)	0.2702(2)	0.0341(9)	0.0313(9)	0.038(1)	0.0058(7)	0.0111(7)	0.0119(7)
C(5)	2*i*	0.3236(3)	1.1700(2)	0.2062(2)	0.037(1)	0.0363(9)	0.045(1)	0.0092(8)	0.0139(8)	0.0117(8)
C(6)	2*i*	0.2116(4)	1.0373(2)	0.1819(2)	0.049(1)	0.0331(9)	0.044(1)	0.0103(8)	0.0135(9)	0.0088(8)
C(7)	2*i*	0.0248(4)	1.0193(2)	0.2247(2)	0.051(1)	0.032(1)	0.054(1)	0.0000(9)	0.013(1)	0.0113(9)
C(8)	2*i*	–0.0590(3)	1.1377(2)	0.2875(2)	0.042(1)	0.039(1)	0.047(1)	0.0004(8)	0.0164(9)	0.0134(9)
C(9)	2*i*	0.0450(3)	1.2721(2)	0.3059(2)	0.0368(9)	0.0336(9)	0.0320(9)	0.0050(7)	0.0104(7)	0.0105(7)
C(10)	2*i*	–0.1370(3)	1.5088(2)	0.2016(2)	0.0306(9)	0.0347(9)	0.039(1)	0.0075(7)	0.0137(7)	0.0080(8)
C(11)	2*i*	0.3484(3)	1.6950(2)	0.3901(2)	0.038(1)	0.0351(9)	0.037(1)	0.0022(8)	0.0072(8)	0.0100(8)
C(12)	2*i*	–0.2150(4)	1.6259(3)	0.0376(3)	0.060(2)	0.069(2)	0.052(2)	0.000(1)	–0.005(1)	0.029(1)
C(13)	2*i*	0.6637(4)	1.8525(2)	0.4209(3)	0.046(1)	0.039(1)	0.078(2)	–0.0080(9)	0.006(1)	0.015(1)

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