Crystal structure of 3-bromo-4-(2-bromo-ethyl)-5-(4-chloro-phenyl)-2-*p*-tolyl-furan, $C_{19}H_{15}Br_2ClO$

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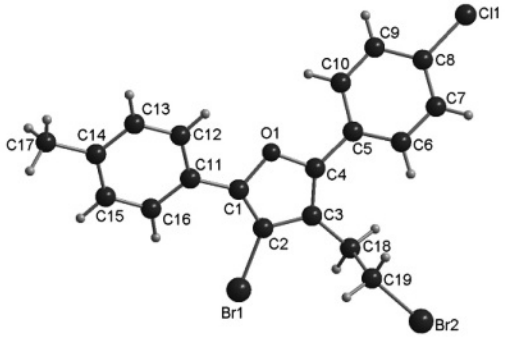

Abstract

$C_{19}H_{15}Br_2ClO$, orthorhombic, $P2_12_12_1$ (no. 19), a = 4.501(2) Å, b = 16.229(8) Å, c = 24.20(1) Å, V = 1767.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.0350, $wR_{ref}(F^2)$ = 0.0637, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.29×0.34×0.41 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	47.39 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8802, 3290
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2094
$N(param)_{refined}$:	209
Programs:	SHELX [13]

Source of material

The title compound was synthesized from the reaction of phenyl-(1-(2-phenylethynyl)cyclopropyl)methanone (0.5 mmol) with copper(II)bromide (3 mmol) in CH_3CN (5 mL). The resulting mixture was stirred at 90 °C for 1 h, then the reaction was quenched with saturated aq. NH_4Cl. The mixture was then extracted with ether and the combined organic layers were dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using hexane as the eluent. The title compound was obtained as a colourless solid.

Experimental details

At the benzene ring, the hydrogen atoms were assigned with $U_{iso}(H) = 1.2\ U_{eq}(C)$, and included in the final refinement by using geometrical restraints, with d(C–H) = 0.93 Å. The hydrogen atoms of the methyl group were assigned with $U_{iso}(H) = 1.5\ U_{eq}(C)$, and included in the final refinement by using geometrical restraints, with d(C–H) = 0.96 Å.

Discussion

Furans represent a class of heterocycles which occur in various natural products and biologically active compounds [1–3]. Moreover, they are also extensively used as an important reaction intermediate for the preparation of a variety of heterocyclic and acyclic compounds [4–6]. In particular, halofurans are of special interest because the halogen atom provide an opportunity for further functionalization by a variety of C–C, C–N, or C–S bond formation through the transition-metal-catalyzed reactions and also serve as building blocks in combinatorial chemistry. As a consequence, a number of efficient and selective methods have been developed for their synthesis. Among many methods developed in past years, the intramolecular electrophilic cyclization of functionally substituted alkynes are the most common synthetic methods for the construction of halofurans, including iodo-cyclization of 3-alkyne-1,2-diols, 2,4-dialkenyl-1,3 -dicarbonyls [7], propargylic oxirane [8], 1,4-disubstituted but-3-yn-1-ones, 2-(1-alkynyl)-alk-2-en-1-ones, (*Z*)-1,4-disubstituted but-1-en-3-ynyl acetates [9]. However, the chlorocyclization and bromocyclization reactions were rarely reported probably because the stability of the corresponding halonium intermediates decreases in the order I>Br>Cl [10–12]. Thus, continuous interest has been directed to the development of new and efficient synthesis of chloro and bromofurans. The crystal structure, determined by X-ray diffraction, reveals that the asymmetric unit is composited of a molecule with three moieties: one furan ring and two benzene rings. While in the furan ring, the bond length of C1–O1, C4–O1 are found to be 1.376(4), 1.366(5) Å, respectively. The bond length of C8–Cl1, C2–Br1 and C19–Br2 are 1.733(5) Å, 1.877(4) Å and 1.928(4) Å. In addition, the dihedral angle between the benzene ring C11 to C16 and the furan ring is 10.31°, the dihedral angle between the benzene ring C5 to C10 and the furan ring is 22.69°, the dihedral angle between the both benzene ring is 31.09°. The bonds connecting the benzene moieties and the furan ring are single bonds, which is confirmed by the bond length of 1.445(6) Å, 1.459(6) Å. Hydrogen bonds between all moieties form a three-dimensional supramolecule.

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

Atom	Site	x	y	z	U_{iso}
H(6)	4*a*	0.9891	0.0967	0.0659	0.078
H(7)	4*a*	1.2278	–0.0051	0.0173	0.081
H(9)	4*a*	1.0664	–0.1621	0.14	0.096
H(10)	4*a*	0.8316	–0.0604	0.188	0.08
H(12)	4*a*	0.2063	–0.0019	0.2639	0.071
H(13)	4*a*	–0.1067	–0.0337	0.3348	0.078
H(15)	4*a*	–0.0378	0.1942	0.3923	0.09

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Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(16)	4*a*	0.2777	0.227	0.3221	0.085
H(17A)	4*a*	–0.1918	0.0427	0.4513	0.108
H(17B)	4*a*	–0.4315	0.0104	0.4096	0.108
H(17C)	4*a*	–0.4304	0.1033	0.4274	0.108

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(18A)	4*a*	1.1145	0.2066	0.116	0.063
H(18B)	4*a*	1.0367	0.2807	0.1552	0.063
H(19A)	4*a*	0.5957	0.303	0.1056	0.074
H(19B)	4*a*	0.6754	0.2293	0.0663	0.074

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*a*	0.5606(1)	0.31348(3)	0.23746(2)	0.0900(4)	0.0512(2)	0.0723(4)	–0.0040(3)	0.0016(3)	–0.0057(2)
Br(2)	4*a*	0.9761(1)	0.34760(3)	0.04113(2)	0.0957(4)	0.0686(3)	0.0697(4)	0.0011(3)	0.0118(4)	0.0231(2)
Cl(1)	4*a*	1.3467(4)	–0.17123(7)	0.03739(6)	0.127(1)	0.0709(8)	0.083(1)	0.0008(8)	0.0337(9)	–0.0145(7)
O(1)	4*a*	0.5661(7)	0.0690(2)	0.2075(1)	0.059(2)	0.051(2)	0.041(2)	–0.006(2)	–0.001(2)	0.001(1)
C(1)	4*a*	0.473(1)	0.1358(2)	0.2380(2)	0.049(3)	0.052(2)	0.045(3)	0.000(2)	–0.008(3)	–0.001(2)
C(2)	4*a*	0.6001(9)	0.2034(2)	0.2149(2)	0.049(3)	0.051(3)	0.045(3)	0.001(2)	–0.007(2)	0.004(2)
C(3)	4*a*	0.7760(9)	0.1804(2)	0.1689(2)	0.046(3)	0.047(3)	0.040(3)	0.000(2)	–0.005(2)	0.010(2)
C(4)	4*a*	0.749(1)	0.0959(3)	0.1661(2)	0.046(3)	0.061(3)	0.039(3)	–0.001(2)	–0.003(3)	0.004(3)
C(5)	4*a*	0.889(1)	0.0315(3)	0.1331(2)	0.054(3)	0.056(3)	0.036(3)	–0.004(2)	–0.001(2)	–0.001(2)
C(6)	4*a*	1.006(1)	0.0446(2)	0.0816(2)	0.090(4)	0.050(2)	0.056(3)	–0.009(3)	0.011(4)	0.006(2)
C(7)	4*a*	1.148(1)	–0.0166(3)	0.0519(2)	0.092(4)	0.059(3)	0.051(4)	–0.007(3)	0.015(3)	0.000(3)
C(8)	4*a*	1.169(1)	–0.0933(3)	0.0735(2)	0.074(4)	0.051(3)	0.055(3)	–0.008(2)	0.011(3)	–0.012(3)
C(9)	4*a*	1.051(2)	–0.1096(3)	0.1249(2)	0.129(5)	0.054(3)	0.057(3)	–0.008(4)	0.022(4)	0.000(3)
C(10)	4*a*	0.913(1)	–0.0484(3)	0.1536(2)	0.101(4)	0.053(3)	0.046(3)	–0.011(3)	0.025(3)	–0.001(2)
C(11)	4*a*	0.276(1)	0.1170(3)	0.2834(2)	0.056(3)	0.051(3)	0.037(3)	0.010(2)	–0.007(3)	0.003(2)
C(12)	4*a*	0.158(1)	0.0386(3)	0.2895(2)	0.067(4)	0.059(3)	0.050(3)	0.004(3)	0.004(3)	–0.006(2)
C(13)	4*a*	–0.029(1)	0.0193(3)	0.3325(2)	0.067(4)	0.068(3)	0.059(3)	–0.006(3)	0.012(3)	0.001(3)
C(14)	4*a*	–0.106(1)	0.0763(3)	0.3722(2)	0.049(3)	0.077(3)	0.055(4)	0.013(3)	0.000(3)	0.019(3)
C(15)	4*a*	0.012(1)	0.1540(3)	0.3665(2)	0.095(4)	0.060(3)	0.069(4)	0.016(4)	0.033(4)	0.003(2)
C(16)	4*a*	0.200(1)	0.1740(3)	0.3239(2)	0.088(4)	0.047(3)	0.077(4)	0.006(3)	0.012(3)	0.004(3)
C(17)	4*a*	–0.308(1)	0.0564(3)	0.4194(2)	0.065(4)	0.089(3)	0.062(4)	0.014(3)	0.011(3)	0.015(3)
C(18)	4*a*	0.952(1)	0.2368(2)	0.1329(2)	0.058(3)	0.050(2)	0.049(3)	–0.005(3)	–0.010(3)	0.006(2)
C(19)	4*a*	0.759(1)	0.2734(3)	0.0885(2)	0.063(3)	0.064(3)	0.059(4)	–0.005(3)	–0.002(3)	0.020(3)

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