Lubabalo Ndima, Jarryd Cuthbertson, Eric C. Hosten and Richard Betz*

Crystal structure of 4-bromobenzaldehyde – complete redetermination at 200 K, C_7H_5BrO

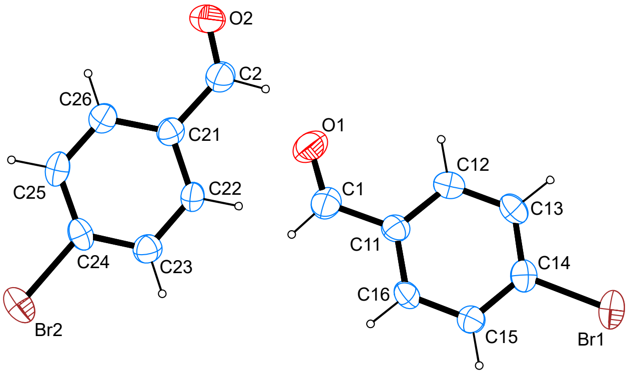

Table 1: Data collection and handling.

Crystal:	Colourless platelet
Size:	$0.58 \times 0.25 \times 0.08$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	6.03 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12490, 3219, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2312
$N(param)_{refined}$:	163
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3], Mercury [4], PLATON [5]

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Abstract

C_7H_5BrO, monoclinic, $P2_1/c$ (no. 14), a = 27.3992(18) Å, b = 3.9369(2) Å, c = 12.8006(8) Å, β = 103.504(2) Å, $V = 1342.60(14)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0469$, $wR_{ref}(F^2) = 0.1103$, T = 200(2) K.

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The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained commercially from Riedel-de-Haen. Crystals suitable for the X-ray diffraction study were obtained unintentionally upon an attempted and failed condensation reaction between the title compound and the diimine derived from the tartaric acid-derived diketone and ammonia in water as the solvent.

Experimental details

The C-bound H atoms were visible on Fourier difference maps but were geometrically placed and refined as riding with $U_{iso}(H) = 1.2\ U_{eq}$ (C) using the appropriate SHELXL AFIX command. Four reflections were omitted from the final refinement owing to poor agreement.

Comment

Imidazole dicarboxylic acid and its substituted derivatives are compounds that have attracted some interest as multidentate ligands due to their ability to give rise to coordination polymers. Especially with aromatic substituents, several coordination compounds of transition metals as well as main group elements have been synthesized and characterized by means of diffraction studies. Among these compounds are, e.g., derivatives featuring strontium [6, 7], lead [7], cadmium

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***Corresponding author: Richard Betz**, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South) University Way, Summerstrand, PO Box 77000, Port Elizabeth, 6031, South Africa, E-mail: Richard.Betz@mandela.ac.za
Lubabalo Ndima, Jarryd Cuthbertson and Eric C. Hosten, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South) University Way, Summerstrand, PO Box 77000, Port Elizabeth, 6031, South Africa

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Br1	0.964709 (19)	0.23970 (15)	0.63578 (4)	0.04366 (16)
Br2	0.535060 (19)	0.76782 (14)	0.17048 (5)	0.04380 (16)
O1	0.78770 (15)	0.6875 (12)	0.1806 (3)	0.0557 (12)
O2	0.71315 (15)	0.2850 (12)	−0.1029 (3)	0.0553 (11)
C1	0.78993 (19)	0.7124 (14)	0.2745 (4)	0.0408 (12)
H1	0.7623	0.8152	0.2953	0.049*
C2	0.71011 (19)	0.2585 (16)	−0.0117 (4)	0.0402 (12)
H2	0.7368	0.1480	0.0371	0.048*
C11	0.83253 (18)	0.5954 (13)	0.3611 (4)	0.0322 (11)
C12	0.87472 (19)	0.4438 (13)	0.3368 (4)	0.0354 (11)
H12	0.8761	0.4122	0.2640	0.042*
C13	0.91430 (19)	0.3399 (14)	0.4182 (4)	0.0373 (12)
H13	0.9431	0.2373	0.4022	0.045*
C14	0.91125 (18)	0.3878 (13)	0.5232 (4)	0.0328 (11)
C15	0.86954 (18)	0.5380 (13)	0.5490 (4)	0.0335 (11)
H15	0.8681	0.5675	0.6219	0.040*
C16	0.83038 (18)	0.6429 (13)	0.4667 (4)	0.0334 (11)
H16	0.8018	0.7484	0.4828	0.040*
C21	0.66723 (18)	0.3870 (13)	0.0311 (4)	0.0314 (10)
C22	0.66899 (18)	0.3459 (13)	0.1392 (4)	0.0340 (11)
H22	0.6972	0.2401	0.1848	0.041*
C23	0.62956 (19)	0.4591 (13)	0.1812 (4)	0.0353 (11)
H23	0.6306	0.4326	0.2554	0.042*
C24	0.58881 (17)	0.6111 (12)	0.1132 (4)	0.0315 (10)
C25	0.58612 (19)	0.6533 (13)	0.0042 (4)	0.0374 (12)
H25	0.5577	0.7567	−0.0415	0.045*
C26	0.62562 (19)	0.5418 (13)	−0.0358 (4)	0.0359 (11)
H26	0.6246	0.5704	−0.1099	0.043*

[a] Occupancy: 0.578(4).

[b] Occupancy: 0.422(4).

[7, 8], manganese [8], cobalt [9], copper [10] as well as several lanthanide elements [11, 12] as central atoms. In a quest to extend the scope of this ligand, it was attempted to synthesize derivatives of phenyl imidazole dicarboxylic acid by condensation of suitably-functionalized benzaldehydes with the diimide derived from tartaric acid and aqueous ammonia according to a published procedure [13]. Although the synthetic protocol outlined was followed meticulously, the crystalline reaction product isolated after attempting the reaction with *para*-bromobenzaldehyde showed only the presence of unreacted aromatic starting material. While the crystal structure of the latter has been reported once, no hydrogen atom coordinates have been deposited or taken into account during the refinement [14]. Apart from this lacking information, the title compound has been found to act as a ligand towards boron in a catalyst [15]. This communication serves to close the gap of a complete description of the title compound, including its hydrogen atoms and pertaining intermolecular interactions.

The title compound is the *para*-brominated derivative of benzaldehyde. The asymmetric unit contains two molecules. The C–Br bond lengths of 1.891(5) and 1.895(5) Å are in good agreement with other carbon–bromine bond lengths on aromatic compounds whose metrical parameters have been deposited with the CSD [16]. Intracyclic C–C–C angles cover a range of 118.6(5)–122.0(5)° in the first molecule and 118.3(5)–122.0(4)° in the second molecule. It is interesting to note that the two extreme values in the first case are found for the carbon atoms in *ortho* and *ipso* position to the bromine atom while in the second case the two extreme values are apparent for the carbon atom in *ortho* and *ipso* position to the formyl group. The least-squares planes as defined by the respective carbon atoms of the aromatic systems in both molecules present in the asymmetric unit intersect at an angle of 10.88(23)°. The formyl groups in both molecules are found nearly in plane with the phenyl group they are bonded to. The angles enclosed by the least-squares planes as defined by the carbon atoms of the respective aromatic system and the three atoms of the formyl group are found at 0.54(23)° and 2.04(39)°. The latter finding can be rationalized by taking into account participation of the formyl groups in resonance stabilization with the aromatic system.

In the crystal, intermolecular C–H…O contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them are apparent. These are supported by the hydrogen atom of the formyl group on one of the two molecules present in the asymmetric unit as donor and the oxygen atom of the formyl group of the second molecule as acceptor. In terms of graph-set analysis [17, 18], the descriptor for these interactions is *D* on the unitary level. Overall, the molecules are connected to isolated dimers. π stacking is not a prominent feature of the crystal structure with the shortest distance in between two centers of gravity found at 3.937(3) Å, a value that corresponds to the length of the crystallographic *b* axis of the compound's unit cell.

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