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

Crystal structure of 4-bromobenzaldehyde – complete redetermination at 200 K, C7H5BrO

Abstract

C7H5BrO, monoclinic, P21/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) Å3, Z = 8, Rgt(F) = 0.0469, wRref(F2) = 0.1103, T = 200(2) K.

CCDC no.: 2027363

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 Uiso(H) = 1.2 Ueq(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 [8], and...
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.

Acknowledgments: The authors thank Nelson Mandela University for financial support.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: None declared.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.
References

1. BRUKER. SAINT, APEX2 and SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.
2. Sheldrick G. M. A short history of SHELX. Acta Crystallogr. 2008, A64, 112–122.
3. Farrugia L. J. WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. 2012, 45, 849–854.
4. Macrae C. F., Bruno I. J., Chisholm J. A., Edgington P. R., McCabe P., Pidcock E., Rodriguez-Monge L., Taylor R., van de Streek J., Wood P. A. Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures. J. Appl. Crystallogr. 2008, 41, 466–470.
5. Spek A. L. Structure validation in chemical crystallography. Acta Crystallogr. 2009, D65, 148–155.
6. Zhang Y., Luo X., Yang Z., Li G. Metal-organic frameworks constructed from imidazole dicarboxylates bearing aromatic substituents at the 2-position. Cryst. Eng. Comm. 2012, 14, 7382–7397.
7. Wang W.-Y., Yang Z.-L., Wang C.-J., Lu H.-J., Zang S.-Q., Li G. 2-Phenyl-4,5-imidazole dicarboxylate-based metal-organic frameworks assembled under hydro(solvo)thermal conditions. Cryst. Eng. Comm. 2011, 13, 4895–4902.
8. Wang W., Niu X., Gao Y., Zhu Y., Li G., Lu H., Tang M. One chiral and two achiral 3-D coordination polymers constructed by 2-phenyl imidazole dicarboxylate. Cryst. Growth Des. 2010, 10, 4050–4059.
9. Xiong Z., Jia H., Ma B., Li G. Syntheses, crystal structures, and properties of three Co(II) supramolecules constructed from phenyl imidazole dicarboxylates. Synth. React. Inorg. Met. Org. Nano-Met. Chem. 2012, 42, 1204–1210.
10. Zhu Y., Wang W.-Y., Guo M.-W., Li G., Lu H.-J. An unprecedented 1-D mixed-valence Cu(II)/Cu(I) metal-organic framework bearing 2-phenyl imidazole dicarboxylates. Inorg. Chem. Commun. 2011, 14, 1432–1435.
11. Chen N., Zhang Y., Yang Z.-L., Li G. Assembly of three 3-D MOFs from 2-phenyl-4,5-imidazole dicarboxylate and oxalate. J. Coord. Chem. 2012, 65, 1221–1231.
12. Li Y.-L., Wang J., Shi B.-B., Li J. A phenyl imidazole dicarboxylate-based 3D terbium-organic framework for selective sensing of nitrobenzene. Supramol. Chem. 2016, 28, 640–646.
13. Lebedev A. V., Lebedeva A. B., Sheludyakov V. D., Kovaleva E. A., Ustinova O. L., Shatunov V. V. Synthesis and N-alkylation of 2-alkyl- and 2-arylimidazole-4,5-dicarboxylic acid esters. Russ. J. Gen. Chem. 2007, 77, 949–953.
14. Britton D. Crystal structures of p-chloro- and p-bromobenzaldehyde. J. Chem. Crystallogr. 1994, 24, 553–556.
15. Hansmann M. M., Melen R. L., Rudolph M., Rominger F., Wadepohl H., Stephan D. W., Hashmi A. S. K. Cyclopropanation/ carboboration reactions of enynes with B(C₆F₅)₃. J. Am. Chem. Soc. 2015, 137, 15469–15477.
16. Allen F. H. The Cambridge Structural Database: a quarter of a million crystal structures and rising. Acta Crystallogr. 2002, B58, 380–388.
17. Bernstein J., Davis R. E., Shimoni L., Chang N.-L. Patterns in hydrogen bonding: functionality and graph set analysis in crystals. Angew. Chem. Int. Ed. Engl. 1995, 34, 1555–1573.
18. Etter M. C., MacDonald J. C., Bernstein J. Graph-set analysis of hydrogen-bond patterns in organic crystals. Acta Crystallogr. 1990, B46, 256–262.