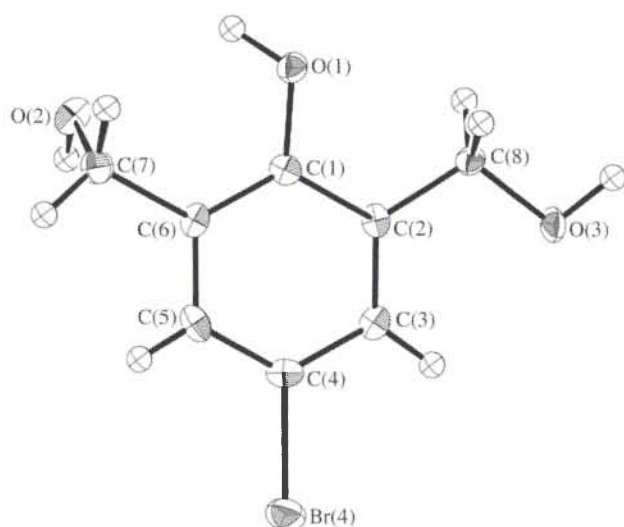


# Crystal structure of 4-bromo-2,6-bis(hydroxymethyl)phenol, $C_8H_9BrO_3$

G. T. Crisp, P. D. Turner and E. R. T. Tiekink\*

The University of Adelaide, Department of Chemistry, Australia 5005

Received January 17, 2000, CCDC-No. 1267/383



## Abstract

$C_8H_9BrO_3$ , monoclinic,  $P12_1/c1$  (No. 14),  $a = 7.365(4)$  Å,  $b = 14.479(4)$  Å,  $c = 8.433(2)$  Å,  $\beta = 112.72(3)^\circ$ ,  $V = 829.5$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{\text{gt}}(F) = 0.029$ ,  $wR_{\text{ref}}(F) = 0.026$ ,  $T = 173$  K.

## Source of material

The title compound was prepared from 4-bromophenol and formaldehyde in the presence of sodium hydroxide according to reference [1]. Colorless needles were obtained from recrystallization from ethyl acetate; mp 423 K – 424 K.

## Discussion

The mean deviation through the least-squares plane defined by the six aromatic carbons, the bromide, the phenolic oxygen and the two methylene carbons is 0.008 Å with the O(2) and O(3) atoms lying 1.312(2) Å and 0.162(2) Å out of this plane, respectively. All hydroxyl groups are involved in both acceptor and donor hydrogen-bonding interactions. Centrosymmetrically related molecules associate via O(1)–H...O(2)*i* interactions implying that while the two molecules are parallel, they are not co-planar as the O(2)H group is not co-planar with the aromatic ring as seen in the C1–C6–C7–O2 torsion angle of 69.7(3)°;  $d(\text{H}\cdots\text{O}(2)i) = 1.75$  Å,  $d(\text{O}(1)\cdots\text{O}(2)i) = 2.663(3)$  Å and the

O(1)–H...O(2)*i* angle is 152°. This association leads to the formation of 12-membered rings. Association with a translationally-related centrosymmetric molecule occurs via O(2)–H...O(3)*ii* interactions such that  $d(\text{H}\cdots\text{O}(3)ii) = 1.76$  Å,  $d(\text{O}(2)\cdots\text{O}(3)ii) = 2.773(3)$  Å and  $\angle\text{O}(2)\text{–H}\cdots\text{O}(3)ii = 163^\circ$ . Sixteen-membered rings result from this pairing of molecules. This also has the result that the two aromatic rings are approximately superimposed and are in close proximity as seen in the average C...C separation of 3.73 Å. Finally, O(3)–H...O(1)*iii* interactions occur:  $d(\text{H}\cdots\text{O}(1)iii) = 1.78$  Å,  $d(\text{O}(3)\cdots\text{O}(1)iii) = 2.802(3)$  Å and  $\angle\text{O}(3)\text{–H}\cdots\text{O}(1)iii = 171^\circ$ . Hence, each molecule is associated with a total of four symmetry-related molecules. The overall structure may be described as being comprised of corrugated layers. Symmetry operations: (i) 1–*x*, –*y*, 2–*z*; (ii) 1–*x*, –*y*, 1–*z*; and (iii) *x*, –0.5–*y*, –0.5+*z*.

Table 1. Data collection and handling.

|                                                         |                                                   |
|---------------------------------------------------------|---------------------------------------------------|
| Crystal:                                                | colourless block,<br>size 0.07 × 0.23 × 0.37 mm   |
| Wavelength:                                             | Mo $K_\alpha$ radiation (0.7107 Å)                |
| $\mu$ :                                                 | 49.31 cm <sup>–1</sup>                            |
| Diffractometer, scan mode:                              | AFC7R, $\omega/2\theta$                           |
| $2\theta_{\text{max}}$ :                                | 55.06°                                            |
| $N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ : | 2125, 1982                                        |
| Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ : | $I_{\text{obs}} > 2\sigma(I_{\text{obs}})$ , 1327 |
| $N(\text{param})_{\text{refined}}$ :                    | 109                                               |
| Programs:                                               | teXsan [2], DIRDIF92 [3], DIFABS [4]              |

Table 2. Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

| Atom  | Site | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}$ |
|-------|------|----------|----------|----------|------------------|
| H(1o) | 4e   | 0.4543   | –0.0870  | 0.8637   | 0.023            |
| H(2o) | 4e   | 0.5765   | 0.1339   | 0.8712   | 0.023            |
| H(3o) | 4e   | 0.3701   | –0.2663  | 0.2643   | 0.023            |
| H(3)  | 4e   | 0.2132   | –0.0361  | 0.1959   | 0.023            |
| H(5)  | 4e   | 0.1642   | 0.1584   | 0.5059   | 0.023            |
| H(7a) | 4e   | 0.2055   | 0.1334   | 0.7980   | 0.023            |
| H(7b) | 4e   | 0.2776   | 0.0290   | 0.8787   | 0.023            |
| H(8a) | 4e   | 0.4888   | –0.1962  | 0.5286   | 0.023            |
| H(8b) | 4e   | 0.2425   | –0.2285  | 0.4664   | 0.023            |

\* Correspondence author (e-mail: edward.tiekink@adelaide.edu.au)

**Table 3.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

| Atom  | Site | <i>x</i>   | <i>y</i>   | <i>z</i>   | <i>U</i> <sub>11</sub> | <i>U</i> <sub>22</sub> | <i>U</i> <sub>33</sub> | <i>U</i> <sub>12</sub> | <i>U</i> <sub>13</sub> | <i>U</i> <sub>23</sub> |
|-------|------|------------|------------|------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Br(4) | 4e   | 0.05852(4) | 0.14483(2) | 0.14077(4) | 0.0279(2)              | 0.0279(1)              | 0.0265(1)              | 0.0101(2)              | 0.0102(1)              | 0.0068(1)              |
| O(1)  | 4e   | 0.3889(3)  | −0.1121(1) | 0.7455(2)  | 0.024(1)               | 0.017(1)               | 0.0160(9)              | −0.0026(8)             | 0.0090(8)              | −0.0002(7)             |
| O(2)  | 4e   | 0.4958(3)  | 0.0893(1)  | 0.9164(2)  | 0.019(1)               | 0.028(1)               | 0.0192(9)              | −0.0104(8)             | 0.0083(8)              | −0.0021(8)             |
| O(3)  | 4e   | 0.3364(3)  | −0.1970(1) | 0.2630(2)  | 0.042(1)               | 0.015(1)               | 0.022(1)               | 0.0012(9)              | 0.0218(9)              | −0.0015(8)             |
| C(1)  | 4e   | 0.3135(4)  | −0.0497(2) | 0.6131(3)  | 0.008(1)               | 0.018(1)               | 0.020(1)               | −0.001(1)              | 0.008(1)               | 0.001(1)               |
| C(2)  | 4e   | 0.2907(3)  | −0.0824(2) | 0.4500(3)  | 0.007(1)               | 0.016(1)               | 0.021(1)               | −0.004(1)              | 0.010(1)               | −0.002(1)              |
| C(3)  | 4e   | 0.2140(4)  | −0.0240(2) | 0.3110(3)  | 0.009(1)               | 0.023(1)               | 0.018(1)               | −0.003(1)              | 0.009(1)               | −0.002(1)              |
| C(4)  | 4e   | 0.1627(4)  | 0.0654(2)  | 0.3353(3)  | 0.010(1)               | 0.023(1)               | 0.019(1)               | 0.000(1)               | 0.007(1)               | 0.006(1)               |
| C(5)  | 4e   | 0.1830(4)  | 0.0974(2)  | 0.4953(3)  | 0.012(1)               | 0.017(1)               | 0.030(1)               | 0.002(1)               | 0.013(1)               | −0.001(1)              |
| C(6)  | 4e   | 0.2606(3)  | 0.0398(2)  | 0.6373(3)  | 0.007(1)               | 0.023(1)               | 0.018(1)               | −0.002(1)              | 0.009(1)               | −0.003(1)              |
| C(7)  | 4e   | 0.2894(4)  | 0.0768(2)  | 0.8120(3)  | 0.018(2)               | 0.021(1)               | 0.022(1)               | 0.004(1)               | 0.011(1)               | −0.001(1)              |
| C(8)  | 4e   | 0.3502(4)  | −0.1804(2) | 0.4344(3)  | 0.021(2)               | 0.016(1)               | 0.015(1)               | −0.002(1)              | 0.009(1)               | 0.001(1)               |

*Acknowledgment.* The Australian Research Council is thanked for support.

## References

1. Moshfegh, A. A.; Mazandarani, B.; Nahid, A.; Hakimelahi, G. H.: 114. The synthesis of hetero-halogenated derivatives of phloroglucide analogues. *Helv. Chim. Acta* **65** (1982) 1229–1232.
2. teXsan: Single Crystal Structure Analysis Software. Version 1.04. Molecular Structure Corporation. The Woodlands, TX, USA 1997.
3. Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C.: The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands 1992.
4. Walker, N.; Stuart, D.: An empirical method for correcting diffractometer data for absorption effects. *Acta Crystallogr. A* **39** (1983) 159–166.