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Short Note

2,2′-(Ethane-1,2-diyl)bis(4-chlorophenol)

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Abstract: The X-ray structure of the title compound, obtained as a byproduct in a natural product synthesis, has been determined and shows an unusual pattern featuring chains of molecules with both intra- and intermolecular hydrogen bonding of the OH groups.

Keywords: X-ray structure; hydrogen bonding

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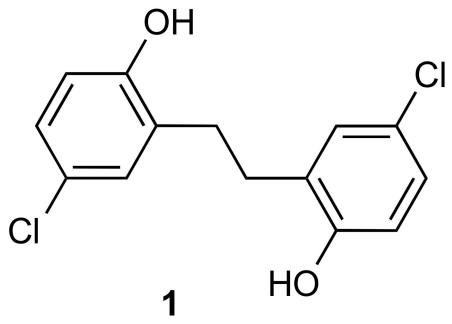
1. Introduction

Some time ago we described the isolation, structure determination and synthesis of an unusual trichlorodihydroxybibenzyl derived from a terrestrial plant native to Trinidad [1]. In the course of the synthesis, the corresponding symmetrical dichlorodihydroxybibenzyl **1** (Figure 1) was obtained as a byproduct and subjected to full spectroscopic characterisation. It was not new, however, since it had already been described much earlier in a 1957 publication by Pfleger and Waldmann [2] and also used in the synthesis of potential herbicides and algicides described in a 1978 patent [3]. Since the arrangement of hydroxyl groups present seemed to offer interesting opportunities for hydrogen bonding, we were interested to investigate this by means of an X-ray structure determination and we describe here the results.



1

Figure 1. Structure of the title compound **1**.

2. Results

The compound was prepared as previously described [1] and was obtained directly by evaporation of a solution in ethanol as colourless prisms suitable for X-ray diffraction. The unit cell contained two closely similar independent molecules (the RMS between the two independent molecules, excluding H atoms is 0.11(1)), each involved in both intramolecular and intermolecular hydrogen bonding (Figure 2). The hydrogen bonding parameters are shown in Table 1.

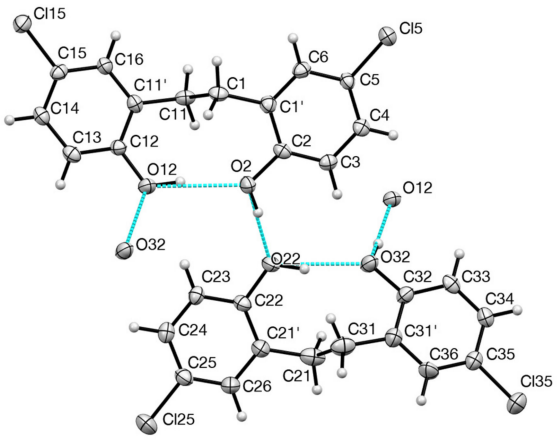


Figure 2. Structure of the two independent molecules showing numbering and the basic hydrogen bonding pattern.

Table 1. Hydrogen bonding parameters for **1** (Å, °).

D—H ... A	D—H	H ... A	D ... A	D—H ... A
O(12)–H(12) ... O(2)	0.84(4)	2.08(4)	2.887(4)	162(5)
O(2)–H(2) ... O(22)	0.84(3)	1.93(4)	2.771(5)	174(4)
O(22)–H(22) ... O(32)	0.84(3)	2.03(3)	2.847(5)	166(5)
O(32)–H(32) ... O(12) [1]	0.84(5)	2.00(5)	2.829(5)	170(7)

[1] Symmetry operator X + 1, Y, Z.

A view of the unit cell along the a axis shows that the molecules form a series of hydrogen-bonded chains oriented in one of two orthogonal directions (Figure 3), and a view along the direction of these chains (Figure 4) clearly shows how the structure is built up by a combination of intra- and intermolecular hydrogen bonding. In terms of the Etter–Bernstein [4] graph set description, these are, respectively, $S(9)$ and $C^2_2(18)$ interactions.

A search of the Cambridge Structural Database (CSD) for 2,2-dihydroxybibenzyl-containing structures shows that the intramolecular $S(9)$ interaction is very uncommon in these, but there is one structure (Refcode LESVEL) that displays this feature: the 2,3-bis(2-hydroxyphenyl)butane **2** [5]. However, rather than a chain as for **1**, this actually forms dimers by an $R^2_2(8)$ interaction (Figure 5).

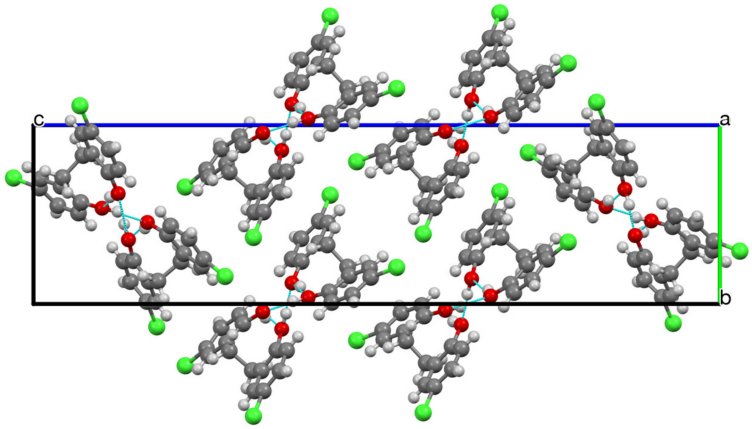


Figure 3. Unit cell viewed along the a axis showing the arrangement of hydrogen-bonded chains.

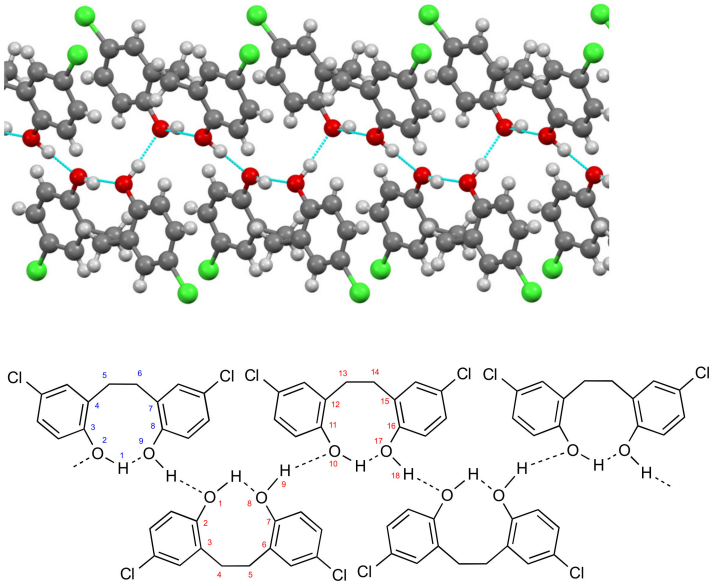


Figure 4. Hydrogen bonding pattern for compound **1** viewed to avoid molecular overlap, together with schematic representation showing derivation of graph set descriptors.

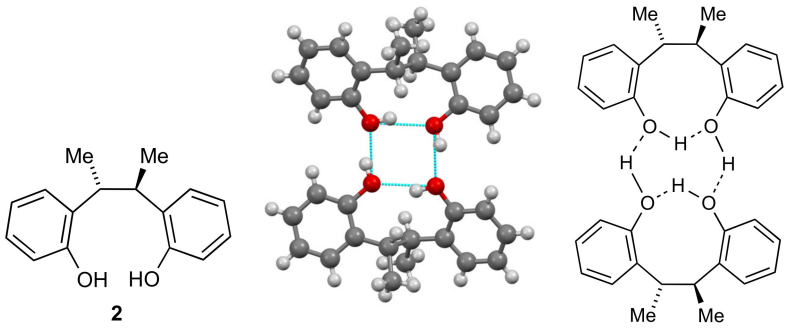


Figure 5. Molecular and crystal structure of **2** [5].

In summary, the X-ray crystal structure of the title compound shows a series of parallel chains formed by intermolecular $C^2_2(18)$ hydrogen bonding interaction of pairs of slightly non-equivalent independent molecules each also featuring an intramolecular $S(9)$ hydrogen bonded ring.

3. Experimental

Crystal data for $C_{14}H_{12}Cl_2O_2$, M = 283.15 g mol^{-1}, colourless prism, crystal dimensions 0.03 × 0.03 × 0.03 mm, monoclinic, space group $P2_1/c$, a = 8.058(3), b = 9.064(3), c = 34.864(12) Å, β = 92.718(11)°, V = 2543.5(16) Å^3, Z = 8, D_{calc} = 1.479 g cm^{-3}, T = 93 K, $R1$ = 0.0698, $Rw2$ = 0.17 for 3205 reflections with $I > 2\sigma(I)$ and 341 variables. There are difference electron density peaks around the molecule containing Cl25 and Cl35 suggesting that there is a molecular disorder such as a C21–C31 crossover (pedal motion) but we were unable to resolve this disorder. The positions of hydrogen atoms bonding to carbon atoms are calculated geometrically and the coordinates and temperature factors are included in the refinement using the riding atom model. The positions of hydrogen atoms bound to oxygen atoms are found from the difference electron density and the coordinates and temperature factors are refined freely. Data were collected using graphite monochromated Mo Kα radiation λ = 0.71075 Å and have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2128951. (Supplementary Materials). The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via

http://www.ccdc.cam.ac.uk/getstructures. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXL, Version 2018/3 [6]).

Supplementary Materials: The following supporting information can be downloaded online, cif and check-cif files for **1**.

Author Contributions: A.L.G.G. prepared the compound; A.M.Z.S. collected the X-ray data and solved the structure; R.A.A. and R.S.R. designed the study; R.A.A. analysed the data and wrote the paper. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The X-ray data are at CCDC as stated in the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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