

Diethyl 2,5-Dihydroxy-3,6-diiodoterephthalate

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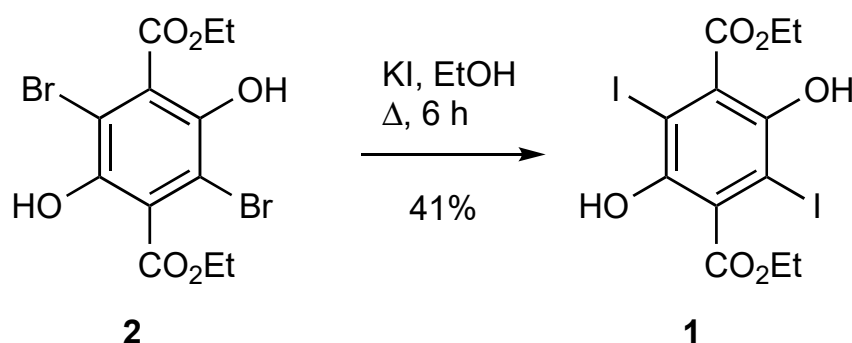
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Abstract: The title compound has been characterised for the first time by the full range of spectroscopic methods, and its X-ray structure shows hydrogen bonded stacks with iodine atoms aligned.

Keywords: X-ray structure; hydrogen bonding

1. Introduction

The simple aromatic compound diethyl 2,5-dihydroxy-3,6-diiodoterephthalate **1** (Scheme 1) was first reported in the literature in 1899 [1]. Rather remarkably, there have been no further references to it since then, and the only experimental data for it is a melting point. In the course of studies on new linkers for metal organic framework (MOF) materials, we prepared the compound, intending to hydrolyse it to give the so-far unknown dihydroxy-diiodoterephthalic acid. In fact, we were unable to hydrolyse **1** to the corresponding diacid, and this prompted further investigation of its structure including analysis by NMR and X-ray diffraction. In this paper, we present full characterisation of **1** for the first time, including UV, IR ^1H and ^{13}C NMR spectra and its X-ray structure (see Supplementary Materials).



Scheme 1. Synthesis and structure of **1**.

2. Results

Compound **1** was readily prepared by reaction of the dibromo analogue **2** [2] with an excess of potassium iodide in boiling ethanol for 6 h. Its UV spectrum (see Supporting Material) showed four strong absorptions in the range 200–354 nm, while its IR spectrum showed a strong C=O absorption at 1686 cm^{-1} . The NMR spectra were in agreement with expectation and featured a ^1H signal at 9.55 ppm for OH as well as a remarkably shielded ^{13}C signal for C–I at 88.6 ppm. This can be compared with a value of 110 ppm for C–Br in compound **2** and results from the well-known heavy atom shielding effect of iodine.

Crystals of compound **1** as prepared were directly suitable for X-ray diffraction, and the resulting molecular structure is shown in Figure 1. This showed the expected high degree of steric congestion around the central six-membered ring, resulting in the ester groups being almost orthogonal to the plane of the benzene ring.



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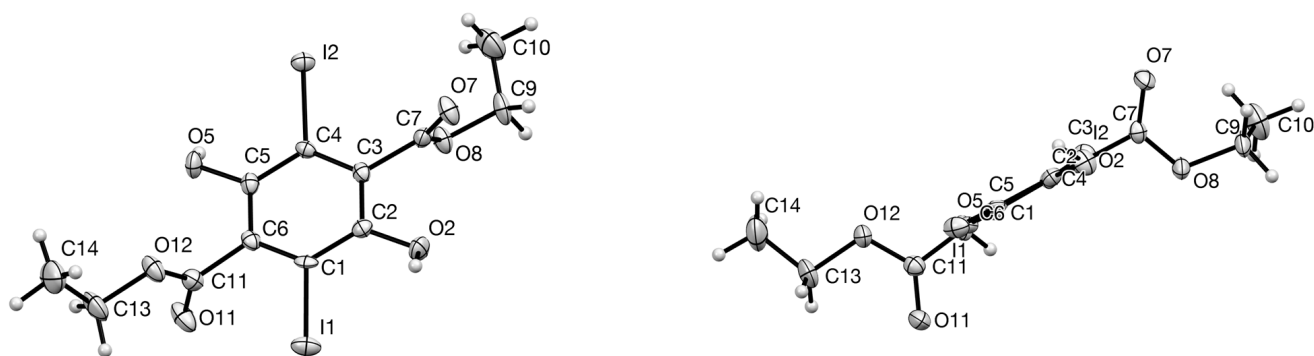


Figure 1. Two views of the molecular structure of **1** showing esters orthogonal to ring (thermal ellipsoids at 50% level). Bond lengths C(1)–I(1) 2.096(3), C(4)–I(2) 2.094(3) Å; torsion angles C(5)–C(6)–C(11)–O(12) $-92.6(4)$, C(2)–C(3)–C(7)–O(8) $109.9(3)$.

In the crystal, adjacent molecules had iodine atoms in a similar orientation but with alternating positions of the hydroxyl and ester groups, allowing efficient hydrogen bonding (Figure 2, Table 1).

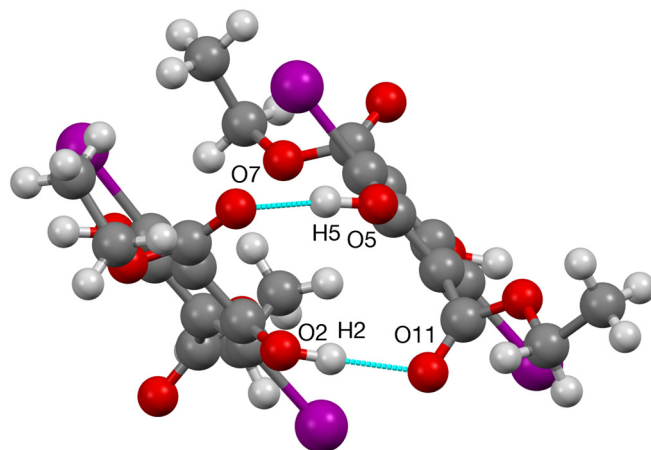


Figure 2. The basic hydrogen bonding pattern.

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

D—H ... A	D—H	H ... A	D ... A	D—H ... A
O(2)–H(2) ... O(11)	0.98(3)	1.90(3)	2.778(4)	149(4)
O(5)–H(5) ... O(7)	0.98(2)	1.79(2)	2.746(3)	163(4)

Overall, the crystal structure consisted of stacks of molecules with the iodine atoms aligned and joined by hydrogen bonds alternately at the top and bottom (Figure 3). This is a type of structure that has been described before for halogenated dihydroxyterephthalate esters. In fact, the solid-state structure of such compounds has been of considerable interest ever since the early observation by Hantzsch of different coloured forms of dimethyl dichlorodihydroxyterephthalate [3]. A summary of the different structures determined for such compounds together with the CSD reference codes and literature references is shown in Figure 4.

In diethyl dihydroxyterephthalate **3**, the molecules are planar and form chains featuring both intra- and intermolecular hydrogen bonding [4]. This is also the case for the dihydro analogue **4**, for which three separate, but essentially identical, structures have been reported [5–7]. Introduction of a bulky substituent such as aryloxy at the remaining ring positions removes the intermolecular hydrogen bonding, and compounds **5–8** retain only the two intramolecular hydrogen bonds [8].

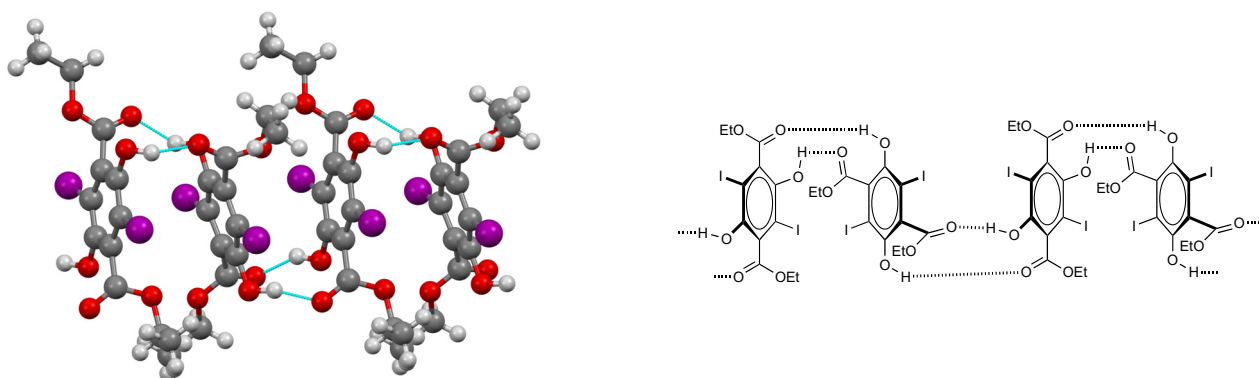


Figure 3. Structure of hydrogen-bonded stacks and schematic representation.

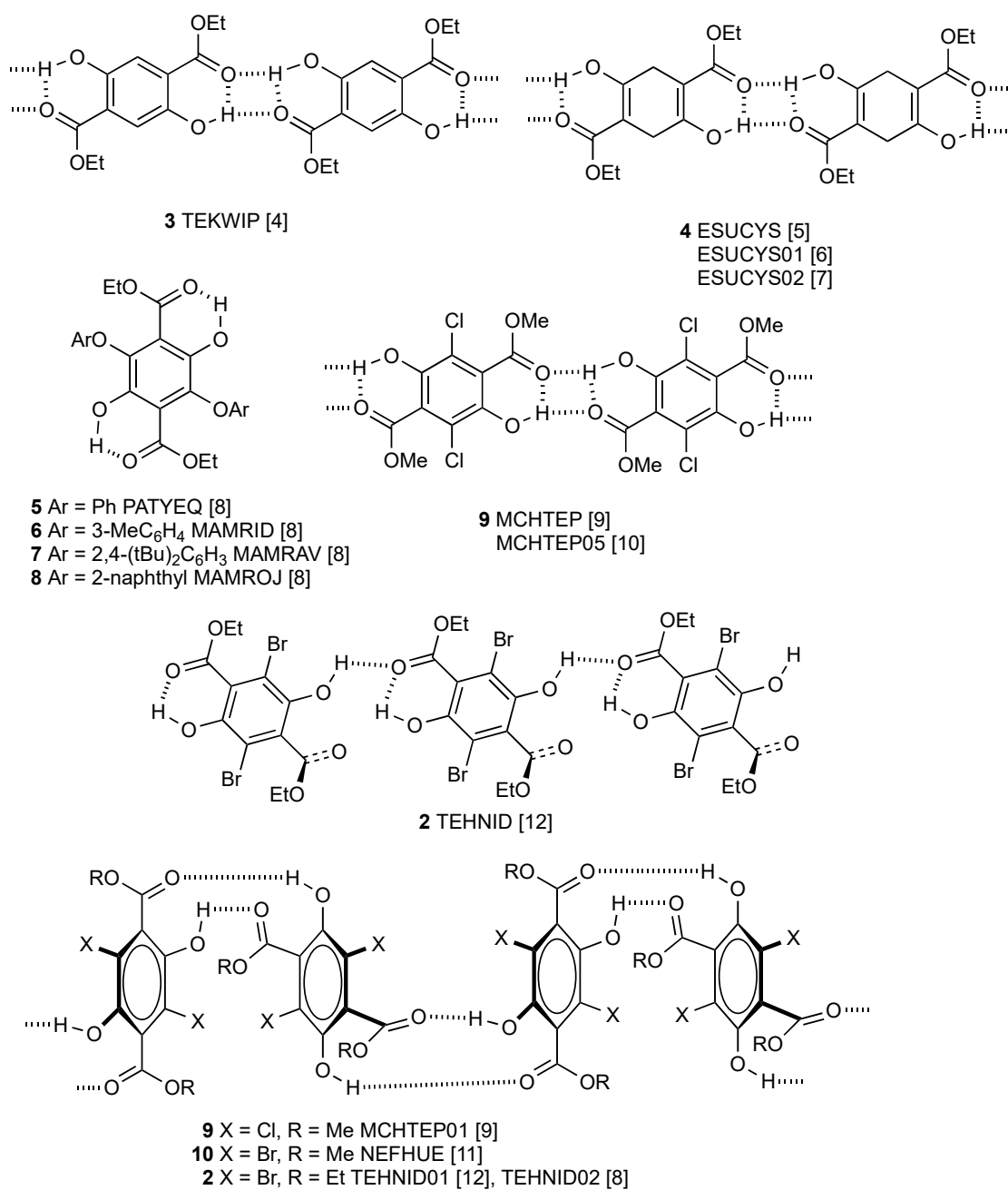


Figure 4. Reported X-ray structures of dihydroxyterephthalates and substituted derivatives [4–12].

When we come to ring halogenated derivatives, the situation is considerably more interesting and provides an explanation on a molecular level for Hantzsch's early observation. Thus, the yellow form of dimethyl dichlorodihydroxyterephthalate **9** has the molecules approximately planar and forming chains featuring both intra- and intermolecular hydrogen bonding, as for **3** and **4** [9]. There is also a further "pale yellow" form that has ester groups twisted out of plane by around 40°, but still retains the same chain structure. However, Hantzsch's white form of **9** has the ester groups orthogonal to the ring with no intramolecular hydrogen bonding, and actually has the same stack structure as we have found for **1** [9]. A similar structure has also been reported for dimethyl dibromodihydroxyterephthalate **10** [11]. When we come to diethyl dibromodihydroxyterephthalate **2**, the situation is slightly different again with two reports of the stack structure lacking intramolecular hydrogen bonding [8,12], but also a different structure that has a chain of molecules in which one ester group is in plane and involved in both intra- and intermolecular hydrogen bonding, but the second ester group is orthogonal and not involved in hydrogen bonding [12].

In summary, the X-ray crystal structure of **1**, the first for a dihydroxydiiodoterephthalate, has the ester groups orthogonal to the benzene ring and adopts the hydrogen bonded stack structure also previously described for the related dichloro and dibromo esters **2**, **9** and **10**.

3. Experimental Section

Melting points were recorded on a Reichert hot-stage microscope (Reichert, Vienna, Austria) and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1420 instrument (Perkin-Elmer, Waltham, MA, USA). NMR spectra were obtained for ¹H at 300 MHz and for ¹³C at 75 MHz using a Bruker AV300 instrument (Bruker, Billerica, MA, USA). Spectra were run at 25 °C on solutions in CD₃SOCD₃ with internal Me₄Si as the reference. Chemical shifts are reported in ppm to high frequency of the reference, and coupling constants *J* are in Hz.

Diethyl 2,5-Dihydroxy-3,6-Diiodoterephthalate (**1**)

A solution of diethyl 3,6-dibromo-2,5-dihydroxyterephthalate **2** [2] (4.0 g, 9.7 mmol) and potassium iodide (4.83 g, 29.1 mmol) in ethanol (40 mL) was heated under reflux for 6 h. The mixture was hot-filtered, and upon cooling to room temperature, a solid was formed which was filtered off and washed with ethanol (3 × 15 mL) to give product **1** (2.0 g, 41%) as faintly pink needles, mp 168–170 °C (lit. [1] 167 °C). UV–Vis (MeCN): λ_{max} (log *e*) 354 (3.85), 290 (4.04), 230 (3.97), 200 (4.04); IR (ATR) 1686 (C=O), 1412, 1306, 1273, 1188, 1142, 1009, 860, 829, 737, 681 cm^{−1}; ¹H NMR (300 MHz, CD₃SOCD₃) 9.55 (2H, br s, OH), 4.30 (4H, q, *J* 7.1), 1.30 (6H, t, *J* 7.1); ¹³C NMR (75 MHz, CD₃SOCD₃) 165.9 (C=O), 146.9 (C–OH), 131.5 (C–CO₂Et), 88.6 (C–I), 61.5 (CH₂), 13.9 (CH₃).

Crystal data for C₁₂H₁₂I₂O₆, *M* = 506.03 g mol^{−1}, colourless plate, crystal dimensions 0.278 × 0.085 × 0.032 mm, orthorhombic, space group Pbca (No. 61), *a* = 8.2343(2), *b* = 18.9496(6), *c* = 19.3066(6) Å, α = β = γ = 90°, *V* = 3012.54(15) Å³, *Z* = 8, *D*_{calc} = 2.231 g cm^{−3}, *T* = 173 K, *R*₁ = 0.0261, *R*_w = 0.0537 for 2594 reflections with *I* > 2σ(*I*), and 191 variables. Data were collected using graphite monochromated Mo Kα radiation λ = 0.71073 Å and have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2,169,373. 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 [13]).

Supplementary Materials: The following are available online. Figure S1: UV–Vis spectrum of **1**; Figure S2: IR spectrum of **1**; Figure S3: ¹H NMR spectrum of **1**; Figure S4: ¹³C NMR spectrum of **1**. Cif and check-cif files for **1**.

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

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