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Spectroscopic, thermal and single crystal structure investigations of 2-bromotrimesic acid and its trimethyl ester analogue

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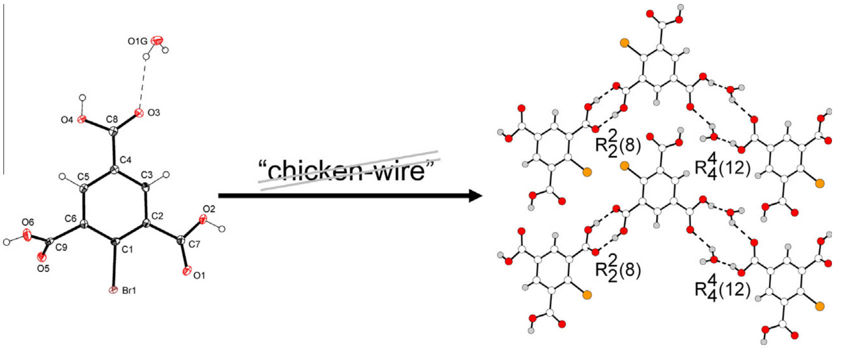
HIGHLIGHTS

- Bromotrimesic acid (**1**) and bromotrimesic trimethyl ester (**2**) were synthesised.
- Single crystal structures were determined to study supramolecular interactions.
- The 1:1 inclusion compound of **1** with water has been investigated by IR spectroscopy and TG-DSC measurements.

GRAPHICAL ABSTRACT



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ABSTRACT

Two analogues of the well investigated trimesic acid *viz.* the 2-bromobenzene-1,3,5-tricarboxylic acid **1** and their ester trimethyl 2-bromobenzene-1,3,5-tricarboxylate **2**, have been synthesised and their X-ray structures were solved. Acid **1** crystallises as 1:1 inclusion compound with water in a layer structure. Like in the solid state structure of trimesic acid, we found strong O—H···O hydrogen bonds between one of the carboxyl groups and a neighbouring molecule to form a hydrogen bonding motif $R_2^2(8)$. Additionally, a water molecule and a second acid function of **1** are involved in further hydrogen bonding featuring the graph set $R_4^4(12)$ forming what might be called a water inserted dimer. As shown by TG-DSC measurements the water molecule in the 1:1 inclusion compound of **1** is engaged in two strong O—H···O hydrogen bonds, it escapes at a rather low temperature of 99 °C. Bromine monosubstitution at the benzene ring forces the third carboxylic acid out of the mean plane of the molecule, which disturbs the coplanar arrangement of the three COOH moieties. Thus, the typical “chicken-wire” network formation is hindered. In the trimethyl 2-bromobenzene-1,3,5-tricarboxylate (**2**), the formation of strong O—H···O hydrogen bonds is disabled by esterification of the acid functions. Nevertheless, the packing of **2** features solvent free molecular layers formed by Br···O contacts and connected van der Waals interactions. These layers are linked to each other by inverse bifurcated hydrogen bonds in term weak C—H···O contacts. The results of the X-ray analysis could be confirmed by infrared spectroscopy.

Introduction

Since its first synthesis in 1867 by Fittig [1] and the single crystal structure determination in 1969 by Duchamp and Marsh [2],

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the interest in trimesic acid (benzene-1,3,5-tricarboxylic acid, TMA) increased dramatically in the last decades. A various number of applications of trimesic acid are conceivably, *e.g.* as a material in dosimeters [3], in spectrofluorimetry for analysing different metal ions, like terbium [4], and as a linker for antibacterial acting metal–organic frameworks [5]. Due to their supramolecular properties and the possibility to form a wide spectrum of metal coordination compounds, trimesic acid can be regarded as a prototype for supramolecular self-assemblies [6,7]. In its guest-free solid state structure TMA forms the so-called "chicken-wire" network induced by a centrosymmetric dimerization of the carboxylic acid groups forming a cyclic hydrogen bonding motif with the graph set $R_2^2(8)$. As a result, voids with a diameter of approximately 14 Å are observed [2]. These supramolecular assemblies are also found in deposited TMA on metal surfaces [8,9]. Besides the structure of the simple trimesic acid, a large number of inclusion complexes are described, *e.g.* clathrates with dimethylamine and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine [10], with dimethyl sulfoxide [11], with water and 1,4-dioxane [12], as well as the respective water complexes $\mathrm{TMA}\cdot\frac{5}{6}\,H_2O$ [11] and $\mathrm{TMA}\cdot 2\,H_2O$ [13], and the inclusion compounds of TMA with water and picric acid [14]. In addition to these, the benzene-1,3,5-tricarboxylate is also known to form metal–organic frameworks [15] with the HKUST-1 [16,17] and MIL-100 [18] as prominent examples and ordinary salts, *e.g.* with rare earth elements [19].

So far, a considerable number of monosubstituted benzene-1,3,5-tricarboxylic acids are described in the literature, such as the 2-amino-[20], 2-methyl-[21], 2-nitro-[22], 2-hydroxy-[23], 2-fluoro-[20], 2-chloro-[24], and 2-methoxybenzene-1,3,5-tricarboxylic acid [25] and their respective esters. However, X-ray data of such monosubstituted trimesic acids are only available for the hydroxyl [26] and carboxy [27] derivatives. In this paper, we describe the synthesis and first comprehensive analytic characterization of 2-bromobenzene-1,3,5-tricarboxylic acid **1** [28,29], and its trimethyl ester, trimethyl 2-bromobenzene-1,3,5-tricarboxylate **2** [28], together with the X-ray structures of **1** as 1:1 inclusion compound with water and the guest-free structure of ester **2**. Additionally, the molecular interactions between **1** and water were investigated by infrared spectroscopy and thermogravimetry coupled with differential scanning calorimetry. Furthermore, the melting behaviour, the heat of fusions, and the infrared spectra of the title compounds have been studied.

Experimental

General experimental and physical measurements

All denoted chemicals are commercially available and were used without further purification. Methanol was subjected to standard drying procedures. ^1H and ^{13}C NMR spectra were recorded (25 °C) with a Bruker Avance III 500 NMR spectrometer at 500.13 MHz and 125.76 MHz, respectively, using DMSO-d_6:D_2O in ratio 1:1 (**1**) and DMSO-d_6 (**2**) as solvents. Chemical shifts (δ) are given in ppm referring to tetramethylsilane as internal standard. The infrared (IR) spectra were obtained from a Varian 3100 FT-IR spectrometer in the region of 4000–450 cm^{-1} (KBr pellet). The thermogravimetric analyses coupled with differential scanning calorimetry (TG-DSC) were performed with a Setaram Sensys TGA DSC under an argon/oxygen flow (20% O_2) of 20 mL/min in the temperature range from 25 to 400 °C using a temperature ramp of 5 K/min.

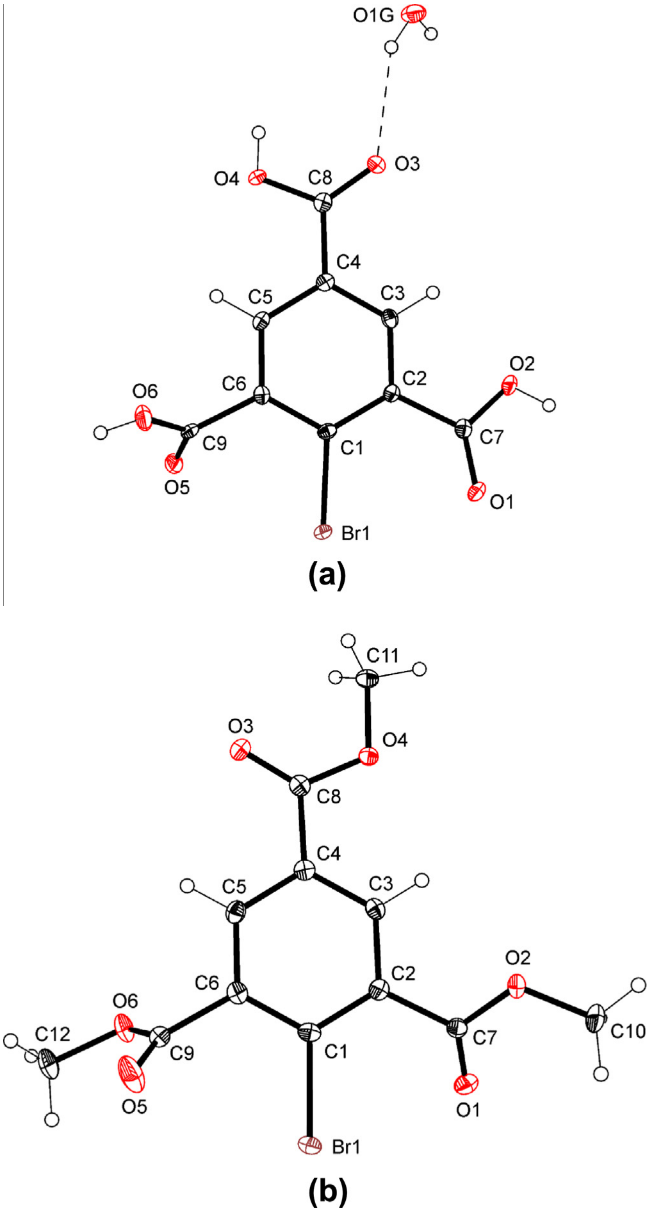
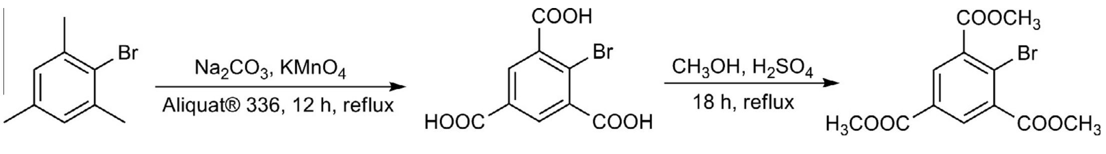


Fig. 2. Molecular diagrams of the title compounds **1** (a) and **2** (b). Thermal ellipsoids are drawn at the 50% probability level.

Synthesis

*2-Bromobenzene-1,3,5-tricarboxylic acid **1***

2-Bromomesitylene (25.1 mmol, 5 g) was suspended in a mixture of Na_2CO_3 (55.5 mmol, 5.88 g) and 2 mL Aliquat® 336 in



1 2

Fig. 1. Scheme of synthesis of compound **1** and **2**.

Table 1
Crystal data and refinement details of the structure determination.

Crystal data	**1**	**2**
Empirical formula	$C_9H_5BrO_6 \cdot H_2O$	$C_{12}H_{11}BrO_6$
Formula weight (g/mol)	307.05	331.11
Crystal description	Colourless needle	Colourless needle
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.9513(4)	8.2399(2)
b (Å)	8.3744(5)	9.0362(2)
c (Å)	8.6638(5)	9.7471(2)
α (°)	114.510(2)	95.9350(10)
β (°)	93.060(2)	111.3160(10)
γ (°)	100.346(2)	107.6560(10)
V (Å^3)	511.082	625.31
Z	2	2
Dc (g cm^{-3})	1.995	1.759
Absorption coefficient (mm^{-1})	4.045	3.307
F (000)	304	332
Crystal size (mm)	0.54 × 0.51 × 0.08	0.39 × 0.18 × 0.16
Data collection		
Temperature (K)	100(2)	100(2)
Radiation, wavelength (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Collected reflections	13,180	13,363
θ Range (°)	2.61–25.00	2.83–24.99
Index ranges $\pm h \pm k \pm l$	−9/9, −9/9, −10/10	−9/9, −10/10, −11/11
Unique data, R_{int}	1790, 0.0401	2195, 0.0198
R_1, wR_2 [$I > 2\sigma$ (I)]	0.0192, 0.0521	0.0148, 0.0378
R_1, wR_2 (all data)	0.0195, 0.0523	0.0151, 0.0379
Refinement		
N_{ref}, N_{par}	1790, 165	2195, 178
Goodness of fit on F^2	1.097	1.090
Max. and av. shift/error	0.001, 0.000	0.001, 0.000
Min. and max. resid. dens. (e Å^3)	−0.436, 0.089	−0.214, 0.311

Table 2
Selected intermolecular hydrogen bonds of the studied structure **1** and **2**.

Atoms involved	Symmetry	Distance (Å)		Angle (°)
		D···A	H···A	D—H···A
1				
O2—H2···O1	−x, 1 − y, 1−z	2.685(2)	1.86(3)	176(3)
O1G—H1G···O3	1 − x, −y, −z	2.930(2)	2.19(1)	146(2)
O4—H4···O1G	x, y, −1 + z	2.566(2)	1.76(3)	163(3)
O1G—H2G···O5	x, −1 + y, z	2.777(2)	1.94(1)	176(2)
O6—H6···O3	x, 1 + y, z	2.644(2)	1.91(3)	161(3)
2				
C10—H10A···O5	1 − x, 1 − y, −z	3.369(2)	2.46	153.9
C11—H11A···O5	x − 1, y − 1, z − 1	3.539(2)	2.58	167.6
C12—H12C···O1	x + 1, y, z + 1	3.522(2)	2.54	176.6
C12—H12B···O2	−1 + x, −1 + y, z	3.390(2)	2.64	133.2

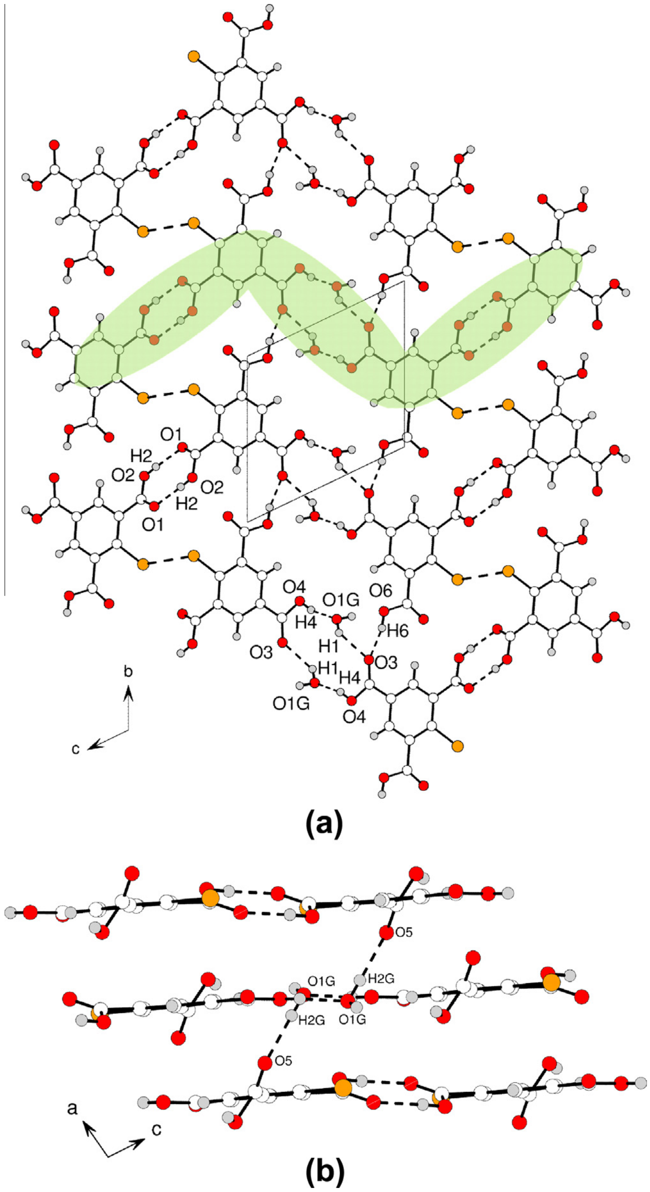


Fig. 3. (a) Layer structure of **1** parallel to the (201) plane with hydrogen bond motifs $R_4^4(12)$ and $R_2^2(8)$, as well as Br···Br contacts. (b) Packing arrangement of **1** viewed down the *b* axis containing O—H···O hydrogen bonds between the layers.

100 mL water and heated to reflux. Potassium permanganate (0.316 mol, 50 g) was added portionwise during a period of 6 h. After an additional reaction time of 6 h (reflux conditions), the excess $KMnO_4$ was destroyed by 25 mL methanol. The formed MnO_2 was separated from the solution and washed three times with water. The combined filtrates were concentrated to half of the original volume and acidified to pH 1 with concentrated hydrochloric acid and extracted thoroughly with diethyl ether (3 × 25 mL). The combined organic phases were washed with water (25 mL), dried over Na_2SO_4, and evaporated to obtain a pale yellow powder. This was purified by recrystallisation using a solvent mixture of tetrahydrofuran and ethanol (5:1) to yield **1** as a white powder (2.07 g, 29%). Mp = 279–282 °C (Lit.: 260–275 °C [28], 276–279 °C [29]). ^{1}H NMR (500.13 MHz, DMSO-d$_6$/D$_2$O, ppm): δ_H = 8.15 (s, Ar—*H*), 13.79 (s, Ar—COO*H*). ^{13}C NMR (125.76 MHz, DMSO-d$_6$/D$_2$O, ppm): δ_C = 166.9, 165.3 (—*C*OOH), 137.1, 130.9, 130.2, 121.5 (Ar—*C*). FTIR (dried sample, KBr, cm^{-1}): $\bar{\nu}$ = 3087, 2978, 2882, 2662, 2546, 1698, 1596, 1412, 1392, 1360, 1290, 1270, 1207, 1178, 1138, 1036, 962, 922, 895, 764, 703, 666, 624, 580, 547, 482.

Trimethyl 2-bromobenzene-1,3,5-tricarboxylate ***2***

Carboxylic acid **1** (3 mmol, 866.7 mg) was dissolved in a mixture of 35 mL dry methanol and 1 mL concentrated sulphuric acid and heated under reflux conditions for 18 h. Subsequently, the methanol was removed by distillation, the residue was diluted in 20 mL water, and extracted with diethyl ether (3 × 25 mL). The combined organic phases were washed with water (25 mL) and dried over Na_2SO_4. Evaporation of the solvent yielded a yellow oil, which was diluted in 10 mL ethanol and cooled in a refrigerator at 7 °C for 12 h, which delivered **2** as colourless needles (0.22 g, 22%). Mp = 96 °C (Lit.: 93–95 °C [28]). ^{1}H NMR (500.13 MHz, DMSO-d$_6$, ppm): δ_H = 8.28 (s, Ar—*H*), 3.90, 3.89 (s, —C*H*$_3$). ^{13}C NMR (125.76 MHz, DMSO-d$_6$, ppm): δ_C = 165.4, 164.1 (—*C*OOCH$_3$), 135.7, 131.9, 129.3, 122.7 (Ar—*C*), 53.0, 52.7 (—COO*C*H$_3$). FTIR (KBr, cm^{-1}): $\bar{\nu}$ = 3461, 3429, 3103, 3074, 3049, 3022, 2954, 2899, 2841, 1741, 1726, 1594, 1582, 1438, 1420, 1404, 1338, 1290, 1243, 1199, 1174, 1138, 1123, 1036, 947, 916, 890, 867, 800, 790, 773, 758, 735, 722, 708, 607, 559, 509, 469.

Single crystal X-ray analysis

The single crystal X-ray diffraction data of compound **1** and **2** were collected at 100 K on a Bruker Kappa diffractometer equipped with an APEX II CCD area detector and graphite-monochromatised Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) employing φ and ω scan modes. The data were corrected for Lorentz and polarization effects. Semi-empirical absorption correction was applied using the SADABS programme [30]. The SAINT programme [30] was used for the integration of the diffraction profiles. The crystal structures were solved by direct methods using SHELXS-97 [31] and refined by full-matrix least-squares refinement against F^2 using SHELXL-97 [31]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the models in calculated positions and were refined as constrained to bonding atoms. Geometrical calculations were performed using PLATON [32] and molecular graphics were generated using SHELXTL [31].

Results and discussion

Synthesis of compounds

The title compounds **1** and **2** were synthesised applying a modified synthesis protocol of Holý et al. [28]. Starting from 2-bromomesitylene compound **1** was synthesised by an oxidation reaction of the methyl groups using potassium permanganate and Aliquat® 336 as a phase transfer catalyst because of the low solubility of the liquid adduct in water. In contrast to the literature the raw product was purified by recrystallisation from a mixture of tetrahydrofuran and ethanol. This procedure leads to the desired tricarboxylic acid (**1**). Trimethyl ester **2** was synthesised using dried methanol and concentrated sulphuric acid similar to a Fischer esterification (Fig. 1). All synthesised compounds were characterised by ^{1}H and ^{13}C NMR spectroscopy, X-ray diffraction, TG-DSC measurements and infrared spectroscopy.

X-ray single crystal analysis

Transparent colourless needles suitable for single crystal X-ray investigations were yielded by slow evaporation of the solvent from a solution of **1** in water/ethanol (5:1) and by refrigerating a solution of **2** in ethanol at 7 °C for 18 h, respectively. The molecular

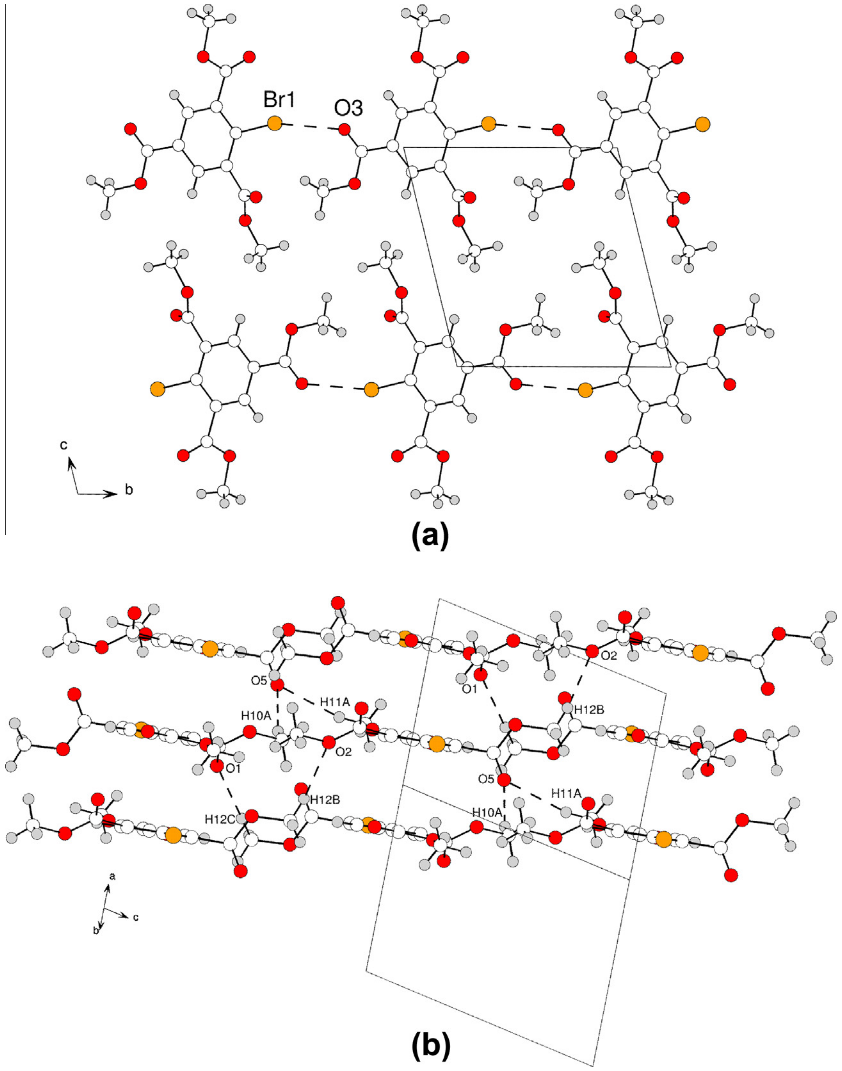


Fig. 4. (a) Br···O contacts in the layer structure of **2**. (b) Packing structure containing C—H···O hydrogen bonds between the molecular layers.

structures of the title compounds are displayed in Fig. 2. Crystal data and details of the structure determination are given in Table 1. The parameter details of the intermolecular interactions are specified in Table 2.

X-ray single crystal analysis of ***1***

2-Bromobenzene-1,3,5-tricarboxylic acid crystallises in the triclinic space group $P\,\bar{1}$, with the unit cell containing one molecule of **1** and one water molecule. The molecular structure is presented in Fig. 2a showing the three carboxyl groups twisted out of the aromatic ring plane, *i.e.* 5.56° (O3—C8—O4), 24.58° (O1—C7—O2), and 56.82° (O6—C9—O5), respectively. In contrast to the typical "chicken wire" network of the trimesic acid [2], the molecules of **1** form a rather different structure. On the one hand two water molecules act as hydrogen donors and acceptors and connect two carboxyl groups of two neighbouring molecules of **1** by strong O—H···O hydrogen bonds [33] [*d*(O4···O1G) = 2.566(2) and *d*(O1G···O3) = 2.930(2) Å] to yield a ring motif with the graph set $R_4^4(12)$. One the other hand two further molecules are directly connected by strong hydrogen bonds between the carboxyl groups [*d*(O2···O1) = 2.6851(19) Å] to form the ring motif $R_2^2(8)$, displayed in Fig. 3a. In the crystal structure the molecules are linked together in direction of the *b* axis by these two different hydrogen bonding schemes leading to a zig-zag pattern. The respective chains are interconnected by strong O—H···O bonds [*d*(O6···O3) = 2.644(2) Å] and Br···Br contacts [*d* = 3.3168(3) Å] [34], resulting in layers parallel to the (2 0 1) plane. Interestingly, by close examination of the hydrogen bonding pattern, we found, that the oxygen O3 forms an inverse bifurcated hydrogen bond to the carboxyl hydrogen H6 and the water hydrogen H1G of the included water molecule. The molecular (2 0 1) layers are linked via strong O—H···O hydrogen bonds [*d*(O1G···O5)] between the heavily twisted carboxyl group (O6—C9—O5) and the water hydrogen H2G (Fig. 3b). Furthermore, π···π interactions among the benzene rings [35] (*d* = 3.795 Å) as well as between the aromatic units and a C═O group (C8═O3) (*d* = 3.321 Å) [36] can be discussed.

X-ray single crystal analysis of ***2***

Trimethyl 2-bromobenzene-1,3,5-tricarboxylate (**2**) crystallises in the same space group as **1** ($P\,\bar{1}$), though the polar protic solvent ethanol is not included. The molecular structure is presented in Fig. 2b showing the three carboxyl groups turned out of the aromatic ring plane as indicated by the interplanary angles of 4.20° (O3—C8—O4), 39.06 (O1—C7—O2), and 66.76° (O6—C9—O5). In comparison to compound **1** the twisting of the acid functions is higher, induced probably by the arrangement of the molecules in absence of solvent molecules in the overall packing. The molecules are assembled in chains along the [1 1 0] direction by Br···O [*d*(Br1···O3) = 3.3387(12) Å]. These chains are oriented oppositely to each other and interconnected only by van der Waals interactions (Fig. 4a). The resulting layers are inclined to the (−1 1 0) plane (20.88°), and held together by aromatic stacking [33] (*d* = 3.620 Å) and interactions between the benzene rings and the C═O group C8—O3 (*d* = 3.527 Å) [34]. In addition, we found weak C—H···O hydrogen bonds [37] between methyl groups and a methoxy oxygen [*d*(C12···O2) = 3.390(2) Å] as well as carbonyl oxygens [*d*(C10···O5) = 3.369(2) Å, *d*(C11···O5) = 3.539(19) Å, *d*(C12···O1) = 3.522(2) Å]. As in **1**, one of the carbonyl oxygens (O5) is engaged in an inverse bifurcated hydrogen bond linked to the methyl hydrogens H10A and H11A (Fig. 4b).

FTIR spectroscopic study of ***1***

Beside the single crystal analyses of the title compounds, their FTIR spectra were recorded. The spectrum of **1** (Fig. 5a) contains the typical bands of the synthesised 2-bromobenzene-1,3,5-tricarboxylic

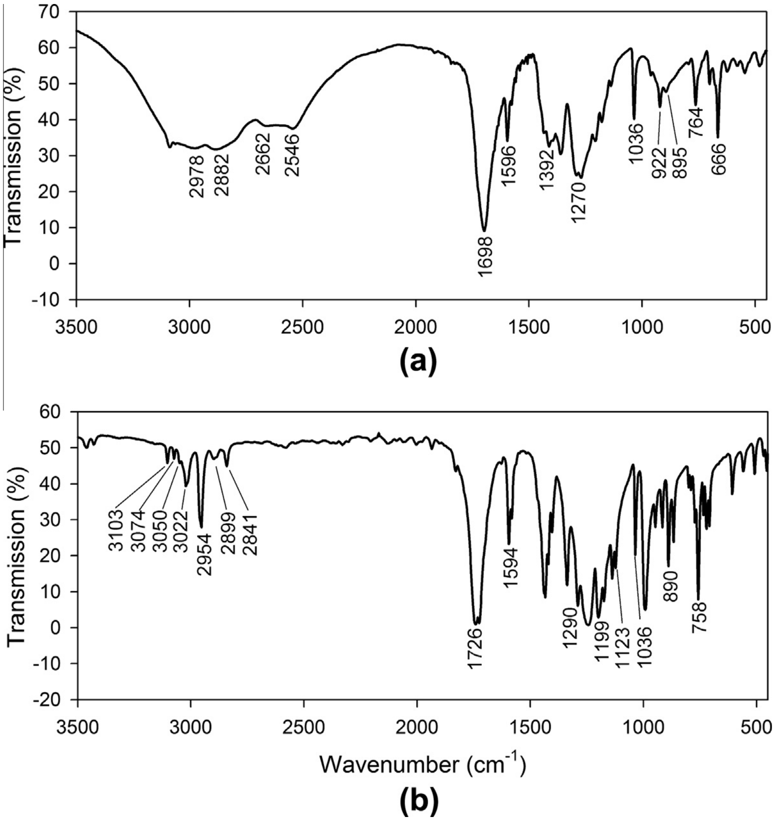


Fig. 5. FTIR spectra of compounds **1** (a) and **2** (b).

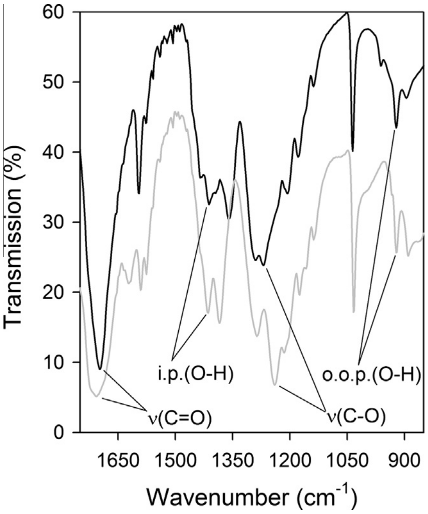


Fig. 6. IR-spectrum of a dried sample of **1** (black line) in comparison to a sample of the single crystal structure analysis of **1** including water in the crystal lattice (grey line) in the range of 1750–850 cm^{-1}.

acid, such as overtone and combination bands between 2662 and 2546 cm^{-1}, aryl-C=O stretch mode at 1698 cm^{-1}, in plane O—H band at 1392 cm^{-1}, C—O vibration at 1270 cm^{-1}, and an out-of-plane O—H band at 922 cm^{-1} indicating the carboxylic acid function. Besides this, typical vibrational modes of the aromatic ring can be found in the spectra of the acid and the ester, including C—H stretches between 3100 and 3000 cm^{-1}, aromatic C=C ring modes at 1596 cm^{-1} in the case of **1** and 1594 cm^{-1} in the case of **2**, as well as the out-of-plane C—H band at 764 cm^{-1} for **1** and 758 cm^{-1} for **2**. The vibration modes at 895 cm^{-1} (**1**) and 890 cm^{-1} (**2**), respectively, indicate the 1,2,3,5-tetra substitution pattern of the synthesised compounds. Furthermore, the bands at 1036 cm^{-1} in the IR spectra of **1** and **2** are aryl-Br stretches and demonstrate the halogen substitution of the aromatic ring, beside the vibrational C—Br band at 666 cm^{-1} in Fig. 5a. In the infrared spectrum Fig. 5b the typical bands of the ester functionalities can be found, such as the intensive C=O stretching mode at 1726 cm^{-1}, the C—C—O band at 1290 cm^{-1}, the O—C—C band at 1123 cm^{-1}, and an asymmetric stretching vibration of the C—O—C bond at 1199 cm^{-1}. The bands between 2954 and 2841 cm^{-1} represent the corresponding asymmetric and symmetric vibrational modes of the methyl groups binding on the oxygen atom of the ester group [38].

The single crystal analysis of compound **1** reveals hydrogen bonds between a water molecule and the carboxyl groups of two different molecules of 2-bromobenzene-1,3,5-tricarboxylic acid. In order to determine the influence of the included solvent on the molecular arrangement of the carboxylic acid functionalities, an IR spectrum of a dried sample of **1** (70 °C, 2 h, vacuum) was recorded in the region from 850 to 1750 cm^{-1}. Hence, we were able to compare its vibrational modes with the corresponding ones of the crystals investigated by the XRD measurements, which can indicate an interaction between the guest molecule and the acid groups. A relative small shift of the C=O and C—O stretching vibrations in the spectrum of the water complex (Fig. 6 grey line) in comparison to the corresponding bands of the dried sample (Fig. 6 black line) underline this fact.

TG-DSC measurements

The thermal stabilities of the synthesised compounds **1** and **2** were investigated by TG-DSC analyses. For the experiment we used 6.88 mg of a dried sample of the 2-bromotrimesic acid (Fig. 7a, black line), 7.20 mg of the complex between water and **1** (Fig. 7a, grey line), and 6.00 mg of the ester **2** (Fig. 7b). The single crystal structure analysis and the infrared spectrum of **1** indicate that acid and water form a 1:1 inclusion compound. Analysing the corresponding TG-DSC measurement a heat effect (α) at 99 °C with an enthalpy of 81.1 kJ/mol has been found as shown in Fig. 7a (grey line). This temperature is close to the boiling temperature of water and pointing to low relative stability [39] of the water inclusion compound of **1**. The corresponding mass loss (β) of 0.437 mg gives an acid to water ratio of 1:1.03 being in a good agreement to the analysis of the single crystal structure (1:1). The grey line of graph (a) shows a further heat effect (γ). Indicated by the low value of 37.9 kJ/mol it presumably belongs to the melting process and not to decomposition. A very broad signal after this well-defined peak indicates the beginning degradation process. For the dried sample (black line, Fig. 7) integration of peak δ delivers an enthalpy of 38.0 kJ/mol, which is in good agreement with the value of the complex between water and **1** (γ). Evaluating both heat effects, melting temperatures of 279 °C (calculated for γ) and 282 °C (calculated for δ) have been determined showing a good conformity between dry **1** and its inclusion compound with water. The literature reports values between 260–275 °C [28] and 276–279 °C [29].

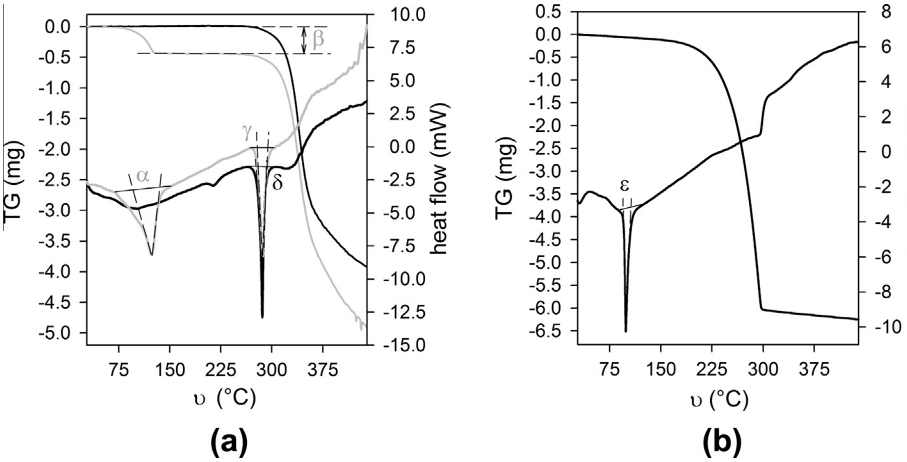


Fig. 7. Thermogravimetric measurements coupled with differential scanning calorimetry of compound **1** (a, black line), **1**·H_2O (1:1) (a, grey line), and ester **2** (b). α Indicates the heat effects of the water release with the corresponding mass loss β and the melting process. The heat effect of the melting of dried **1** is labeled with δ, of the clathrate with γ, and of **2** with ε.

Fig. 7b displays the TG-DSC measurement of the synthesised ester compound **2**. A melting effect of 29.9 kJ/mol at a temperature of 96 °C labelled with (ε) is observed in comparison to a melting point of 93–95 °C presented by Holý et al. [28]. In addition, a decomposition accompanied by an intensive mass loss starting at 170 °C is detected.

Conclusions

In this contribution, we present two of the first single crystal structures of a simple monosubstituted derivative of the well-investigated trimesic acid. The influence of the two different functional groups, carboxylic acid and ester, on the arrangement of the crystal packing was investigated by a X-ray study. Our analyses demonstrate, that **1** crystallises as 1:1 inclusion compound with water in a layer structure. Like in the solid state structure of trimesic acid, we found strong O—H···O hydrogen bonds between one of the carboxyl groups and a neighbouring molecule to form a hydrogen bonding motif $R_2^2(8)$. Additionally, a water molecule and a second acid functions of **1** are involved in further hydrogen bonding featuring the graph set $R_4^4(12)$ forming what might be called a water inserted dimer. Bromine monosubstitution at the benzene ring forces the third carboxylic acid out of the mean plane of the molecule, which disturbs the coplanar arrangement of the three COOH moieties. Thus, the typical "chicken-wire" network formation is hindered. In the trimethyl 2-bromobenzene-1,3,5-tricarboxylate (**2**), the formation of strong O—H···O hydrogen bonds is disabled by esterification of the acid functions. Nevertheless, the packing of **2** features solvent free molecular layers formed by Br···O contacts and connected van der Waals interactions. These layers are linked to each other by inverse bifurcated hydrogen bonds in term weak C—H···O contacts. The results of the X-ray analysis could be confirmed by infrared spectroscopic and TG-DSC measurements. Despite the water molecule in the 1:1 inclusion compound of **1** is engaged in two strong O—H···O hydrogen bonds, it escapes at a rather low temperature of 99 °C.

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Appendix A. Supplementary material

The crystallographic information files have been deposited by using the Cambridge structure database (CCDC 994928, CCDC 994929). These data can be obtained free of charge via www.ccdc.cam.ac.uk/datarequest/cif, by e-mailing data-request@ccdc.com.ac.uk or by contacting the Cambridge CB21 EZ, U.K.; Fax, +44 1223 336033. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.06.035.

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