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Little change but great effect: varying supramolecular interactions in 2,5-dimethoxyterephthalic acid and 2,5-diethoxyterephthalic acid

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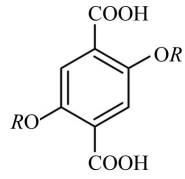
The title terephthalic acid derivatives, namely 2,5-dimethoxyterephthalic acid, $C_{10}H_{10}O_6$, (I), and 2,5-diethoxyterephthalic acid, $C_{12}H_{14}O_6$, (II), exhibit nearly planar molecular structures, with maximum deviations from the least-squares planes calculated for all non-H atoms of 0.0418 (6) and 0.0902 (10) Å for (I) and (II), respectively. The molecules of both title compounds contain an inversion centre and thus the asymmetric unit of both crystal structures consists of only half a molecule. It is a remarkable fact that a comparatively small change in the substitution of the terephthalic acid [dimethoxy in (I) *versus* diethoxy in (II)] causes major differences in the dominating supramolecular interactions. While in (II) the packing structure is stabilized by typical intermolecular hydrogen-bonded carboxylic acid dimer interactions, the carboxyl group in (I) forms an unusual intramolecular hydrogen bond with the O atom of the neighbouring methoxy group.

Comment

Over recent years, much importance has been attached to the synthesis of di-, tri- and tetracarboxylic acids, aiming at applications in the field of structural chemistry. This may be due to the utilization of appropriate carboxylates as linker molecules for the generation of metal–organic frameworks (MOFs) (Chui *et al.*, 1999; Eddauodi, Kim, Rosi *et al.*, 2002; Farha *et al.*, 2010). One point of interest is the introduction of functional groups into MOF structures, facilitating specific applications such as catalysis (Shultz *et al.*, 2009), separation (Chen *et al.*, 2006) or gas storage (Rosi *et al.*, 2003). For this purpose, owing to their easy accessibility, derivatives of terephthalic acid are frequently used. An outstanding challenge is the formation of MOF structures with the same precision as practised in organic synthesis. Therefore, knowledge of the exact geometry of the linker molecules is very important, since their structures have a major influence on the topology of the framework structure formed during MOF synthesis (*e.g.* Böhle *et al.*, 2011*a*,*b*). Notably, small modifications of the terephthalic acid structure, such as the introduction of space-filling substituents, can lead to a distortion of the carboxylate docking groups and thus change the geometric configuration (Eddaoudi, Kim, O'Keeffe *et al.*, 2002). We report here the remarkable structural behaviour of two alkoxy-substituted dicarboxylic acids, namely 2,5-dimethoxyterephthalic acid, (I), and 2,5-diethoxyterephthalic acid, (II), which have already been shown to exhibit flexible coordination modes as linker molecules in MOF structures (Böhle *et al.*, 2011*a*,*b*).



(I) R = Me
(II) R = Et

Both title compounds crystallize in monoclinic space groups, *viz.* $C2/c$ for (I) and $P2_1/n$ for (II), with the asymmetric unit containing half a molecule of the respective title compound. The molecular structures of (I) and (II) are shown in Fig. 1. The bond lengths of the aromatic core are in the range 1.3891 (14)–1.4003 (14) Å for (I) and 1.3932 (14)–1.4056 (15) Å for (II) and thus do not vary significantly from each other, which is also the case for the bond angles of the aromatic system [119.43 (9)–120.77 (9)° for (I) and 118.21 (10)–122.38 (10)° for (II)]. A remarkable feature of both compounds is the nearly planar molecular geometry, characterized by maximum deviations from the least-squares planes calculated for all non-H atoms of 0.0418 (6) (atom O1) and 0.0902 (10) Å (atom C5) for (I) and (II), respectively. A completely planar arrangement of the molecules is not found as the carboxy group is slightly distorted with reference to the aromatic ring, which can be concluded from the dihedral angles between the respective mean planes [2.55 (16)° for (I) and 2.89 (14)° for (II)]. This slight deviation from an ideal coplanarity is also found for unsubstituted terephthalic acid in its different polymorphic structures [triclinic I (Bailey & Brown, 1967), triclinic II (Domenicano *et al.*, 1990) and monoclinic (Śledź *et al.*, 2001)].

In comparision with unsubstituted terephthalic acid, the hydrogen-bonding arrangement in (I) seems to be uncommon, as the carboxyl groups form intramolecular hydrogen bonds [$S(6)$ graph-set motif (Etter, 1990)] with a neighbouring methoxy group (O2—H2···O3) (Fig. 1*a*), and do not interact with the carboxyl groups of neighbouring molecules (Fig. 2) in order to form typical hydrogen-bonded carboxylic acid dimers (Jeffrey, 1997) of $R_2^2(8)$ synthon mode (Etter, 1990). This is, however, the case for (II), where the molecules are linked to each other *via* intermolecular hydrogen-bonding interactions (O1—H1···O2^{iv}; see Table 2 for symmetry code), leading to

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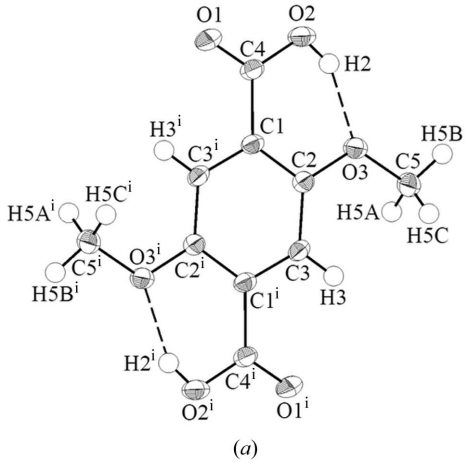
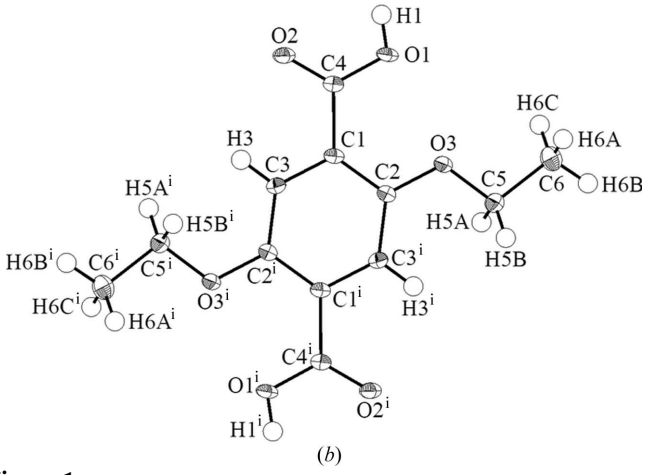


(*a*)



(*b*)

Figure 1
The molecular structures of (*a*) 2,5-dimethoxyterephthalic acid, (I), and (*b*) 2,5-diethoxyterephthalic acid, (II). Displacement ellipsoids are drawn at the 50% probability level. Dashed lines represent intramolecular hydrogen-bonding interactions. [Symmetry code: (i) $-x, -y+2, -z$.]

the formation of one-dimensional strands within the packing structure (Fig. 3). A consideration of crystal structures of similar compounds shows that the mode of interaction of the carboxyl groups does not depend on the substitutent (methoxy *versus* ethoxy) but is probably caused, to a greater extent, by packing effects. Thus, in the structures of 2-methoxybenzoic acid (Parvez, 1987) and 2-ethoxybenzoic acid (Gopalakrishna & Cartz, 1972), a carboxylic acid dimer is formed in the case of the methoxy derivative, while an intramolecular hydrogen bond is observed for the ethoxy-substituted benzoic acid.

The structures of both (I) and (II) exhibit offset face-to-face π–π stacking interactions (Hunter & Sanders, 1990; Salonen *et al.*, 2011). Since in the packing of (I) the carboxyl groups do not contribute to the formation of a characteristic packing motif, π–π stacking, as a weaker intermolecular interaction, comes to the fore. Thus, in the packing of methoxy derivative (I) the aromatic systems are stacked in the direction of the crystallographic *c* axis (Fig. 2), with a centroid-to-centroid distance of 3.8277 (5) Å and a perpendicular centroid-to-plane distance of 3.4149 (4) Å. These interactions are reinforced by weak (methyl)C—H···O interactions (C5—H5*A*···O1^{ii} and C5—H5*B*···O1^{iii}; see Table 1 for symmetry codes) between different π-stacks (Fig. 2). The packing structure of (II) is dominated by the carboxylic acid dimer interaction discussed above. Nevertheless, offset face-to-face π–π stacking [centroid-to-centroid distance = 3.9796 (7) Å and perpendicular centroid-to-plane distance = 3.3201 (5) Å] occurs in the direction of the crystallographic *a* axis (Fig. 3).

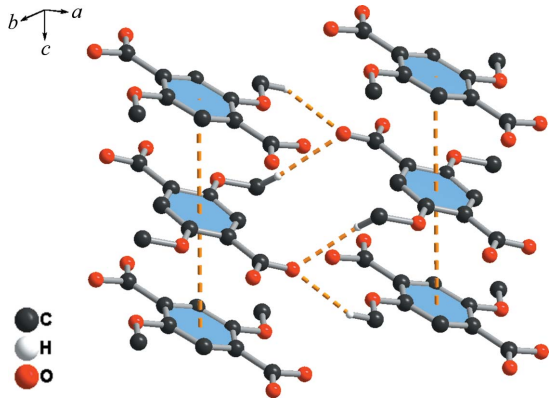


Figure 2
A packing diagram for (I). Thick dashed lines indicate hydrogen bonds and π–π stacking interactions. Intramolecular hydrogen bonds and H atoms not involved in hydrogen bonding have been omitted for clarity.

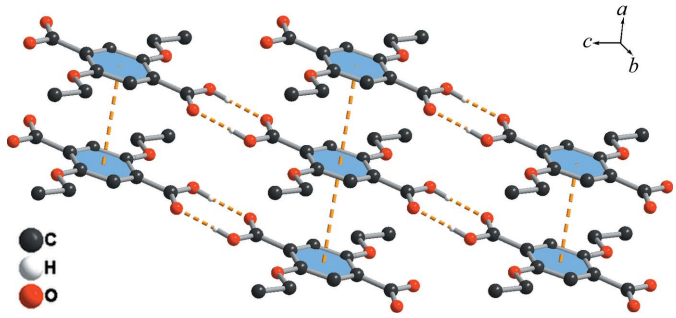


Figure 3
A packing diagram for (II). Hydrogen bonding and π–π stacking interactions are represented as thick dashed lines. H atoms not involved in hydrogen bonding are omitted for clarity.

Experimental

The two title compounds have been synthesized by an alkylation–saponification procedure starting from diethyl 2,5-dihydroxyterephthalate. 2,5-Dimethoxyterephthalic acid, (I), was synthesized according to a modification of the literature procedure of Passaniti *et al.* (2002) by refluxing diethyl 2,5-dihydroxyterephthalate (1.0 g, 4.1 mmol) and methyl iodide (1.3 ml, 20.7 mmol) in a suspension of K_2CO_3 (2.85 g, 20.7 mmol) and dry acetone (20 ml) for 48 h. To remove excess methyl iodide, methanol (15 ml) was added and the suspension refluxed for a further 48 h. After cooling the reaction mixture to room temperature, the remaining solid residue was filtered off and diethyl 2,5-dimethoxyterephthalate was precipitated by the addition of water. Compound (I) was obtained by refluxing diethyl 2,5-dimethoxyterephthalate in a tenfold amount of an aqueous 30% KOH solution for 12 h. After cooling the reaction mixture to room temperature, 6 *M* HCl was added to cause precipitation of the

product, which was washed with water and dried at 373 K for 12 h (yield 76%, m.p. 538 K). ^{1}H NMR (DMSO-d_6, 500.13 MHz): δ 3.79 (*s*, 6H, CH_3), 7.30 (*s*, 2H, Ar–*H*), 13.02 (*s*, *br*, 2H, O*H*); ^{13}C NMR (DMSO-d_6, 125.76 MHz): δ 56.7 (*C*H$_3$), 114.8 (Ar*C*–COOH), 125.4 (Ar*C*–H), 151.4 (Ar*C*–OCH$_3$), 167.1 (*C*OOH).

2,5-Diethoxyterephthalic acid, (II), was synthesized according to the procedure described above but using ethyl iodide (1.7 ml, 20.7 mmol) instead of methyl iodide for the alkylation step (yield 81%, m.p. 523 K). ^{1}H NMR (DMSO-d_6, 500.13 MHz): δ 2.28 (*t*, 6H, CH_3, $^3J_{HH}$ = 7.1 Hz), 4.20 (*q*, 4H, CH_2, $^3J_{HH}$ = 7.0 Hz), 7.24 (*s*, 2H, Ar–*H*), 12.95 (*s*, *br*, 2H, O*H*); ^{13}C NMR (DMSO-d_6, 125.76 MHz): δ 15.1 (*C*H$_3$), 65.4 (*C*H$_2$), 116.1 (Ar*C*–COOH), 126.1 (Ar*C*–H), 150.7 (Ar*C*–OCH$_2$CH$_3$), 167.3 (*C*OOH).

Crystals of (I) and (II) suitable for X-ray crystallographic determinations were afforded by slow evaporation of the solvent from solutions in acetone.

Compound (I)

Crystal data

$C_{10}H_{10}O_6$
M_r = 226.18
Monoclinic, *C*2/*c*
a = 11.6424 (3) Å
b = 10.7368 (3) Å
c = 7.6554 (2) Å
β = 93.804 (2)°
V = 954.83 (4) Å^3
Z = 4
Mo *K*α radiation
μ = 0.13 mm^{-1}
T = 153 K
0.45 × 0.18 × 0.13 mm

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.915, T_{max} = 0.983
5259 measured reflections
985 independent reflections
869 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.084
S = 1.10
985 reflections
75 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Compound (II)

Crystal data

$C_{12}H_{14}O_6$
M_r = 254.23
Monoclinic, $P2_1/n$
a = 3.9796 (2) Å
b = 15.7498 (7) Å
c = 9.3833 (4) Å
β = 98.829 (1)°
V = 581.16 (5) Å^3
Z = 2
Mo *K*α radiation
μ = 0.12 mm^{-1}
T = 153 K
0.25 × 0.22 × 0.04 mm

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.926, T_{max} = 0.995
5854 measured reflections
1331 independent reflections
1134 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.089
S = 1.06
1331 reflections
84 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3	0.84	1.81	2.5720 (10)	150
C5—H5*A*···O1^{ii}	0.98	2.58	3.4634 (14)	150
C5—H5*B*···O1^{iii}	0.98	2.46	3.1718 (13)	129

Symmetry codes: (ii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{iv}	0.84	1.80	2.6394 (11)	177

Symmetry code: (iv) $-x+1, -y+2, -z+1$.

For both compounds, H atoms were positioned geometrically and allowed to ride on their respective parent atoms, with C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl, C—H = 0.99 Å and U_{iso}(H) = 1.2U_{eq}(C) for methylene, C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for aryl, and O—H = 0.84 Å and U_{iso}(H) = 1.5U_{eq}(O) for carboxy H atoms.

For both compounds, data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3074). Services for accessing these data are described at the back of the journal.

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