The crystal structures of four dimethoxybenzaldehyde isomers

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The crystal structures of four dimethoxybenzaldehyde (C₉H₁₀O₃) isomers, namely the 2,3-, 2,4-, 2,5- and 3,5- isomers, are reported and compared to the previously reported crystal structures of 3,4-dimethoxybenzaldehyde and 2,6-dimethoxybenzaldehyde. All dimethoxybenzaldehyde molecules in the crystal structures are nearly planar. The largest deviation (1.2 Å) from the aromatic plane is found for one of the methoxy groups of 2,3-dimethoxybenzaldehyde. Upon rapid cooling of 3,4-dimethoxybenzaldehyde and 3,5-dimethoxybenzaldehyde, a metastable polymorph is formed. The crystal studied for the 3,5- isomer was refined as a two-component twin.

1. Chemical context

Dimethoxybenzaldehydes (DMBz) are often used as starting materials in condensation reactions forming Schiff base compounds. Schiff base compounds are versatile ligands in numerous metal–organic complexes that are used as a catalyst. Examples include C—O coupling reactions (Maity et al., 2015), the Suzuiki–Miyaura reaction (Das & Linert, 2016), nitroaldol reactions (Handa et al., 2008) and a wide variety of other reactions (Gupta & Sutar, 2008).

Whereas the crystal structures of nearly 100 DMBz derivatives have been published, not all of the crystal structures of the DMBz starting compounds are known. Only the crystal structures of 3,4-DMBz (de Ronde et al., 2016) and 2,6-DMBz (Lemercier et al., 2014) have been reported. In this work, we report the structures of the four other dimethoxybenzaldehyde isomers, namely 2,3-DMBz (Fig. 1), 2,4-DMBz (Fig. 2), 2,5-DMBz (Fig. 3) and 3,5-DMBz (Fig. 4).
2. Structural commentary

All four reported isomers crystallize in the monoclinic space group \(P_2_1/c\), which is also the case for the previously reported 2,6-DMBz (Lemercier et al., 2014). On the other hand, 3,4-DMBz was reported to crystallize in space group \(Pna_2_1\) (de Ronde et al., 2016). 3,5-DMBz has two molecules in the asymmetric unit, while the other crystal structures have one molecule in the asymmetric unit. The DMBz molecules in the crystal structures are almost planar (Table 1). The biggest deviation is found in the 2,3-DMBz in which one of the methoxy groups deviates by 1.2 Å from the aromatic plane.

3. Supramolecular features

In the crystal structure of 2,3-DMBz, one of the methoxy groups lies in the plane of the aromatic ring (see Fig. 5). The second methoxy group points towards the aldehyde group of a neighboring 2,3-DMBz molecule. In the crystal structure of 2,4-DMBz, shown in Fig. 6, \(\pi-\pi\) stacking interactions between the aromatic rings are present along the \(b\)-axis direction [centroid–centroid separation = 3.9638 (2) Å]. Similarly, in the crystal structure of 2,5-DMBz, aromatic \(\pi-\pi\) stacking interactions are present along the \(a\)-axis direction [centroid–centroid separation = 3.8780 (3) Å], as shown in Fig. 7. The crystal structures of 2,6-DMBz (Lemercier et al., 2014), 3,4-DMBz (de Ronde et al., 2016) and 3,5-DMBz do not exhibit aromatic \(\pi-\pi\) stacking interactions. As mentioned

### Table 1

Deviation from the aromatic plane (in Å).

|               | 2,3-DMBz | 2,4-DMBz | 2,5-DMBz | 2,6-DMBz (CSD refcode: LIZLAJ) | 3,4-DMBz (CSD refcode: IQUGUY) | 3,5-DMBz (molecule 1) | 3,5-DMBz (molecule 2) |
|---------------|----------|----------|----------|-------------------------------|-------------------------------|-----------------------|-----------------------|
| Aldehyde C    | 0.020    | 0.060    | 0.004    | 0.027                         | 0.020                        | 0.027                 | 0.022                 |
| Aldehyde O    | 0.104    | 0.089    | 0.113    | 0.015                         | 0.095                        | 0.019                 | 0.047                 |
| Methoxy 1 O   | 0.048    | 0.013    | 0.033    | 0.011                         | 0.002                        | 0.009                 | 0.015                 |
| Methoxy 1 C   | 1.200    | 0.122    | 0.099    | 0.017                         | 0.001                        | 0.087                 | 0.258                 |
| Methoxy 2 O   | 0.035    | 0.019    | 0.025    | 0.024                         | 0.033                        | 0.013                 | 0.019                 |
| Methoxy 2 C   | 0.013    | 0.074    | 0.109    | 0.040                         | 0.337                        | 0.020                 | 0.109                 |

Methoxy 1 and 2 are defined in the same order as the atomic labels, as shown in Fig. 4.
above, only 3,5-DMBz has two molecules in the asymmetric unit, whereas the other crystal structures have one molecule in the asymmetric unit.

4. Polymorphism

Polymorph screening using differential scanning calorimetry did not reveal any phase transitions for any DMBz between 133 K and the melting point of the compound (Table 2). On the other hand, a metastable polymorphic form was discovered after rapidly cooling from the melt for both 3,4-DMBz for which the crystal structure was reported previously (de Ronde et al. 2016) and 3,5-DMBz. In the course of hours, these polymorphic forms transformed into the stable forms. Powder X-ray diffraction measurements confirmed the existence of these metastable forms (3,4-DMBz: Figs. 8, 3, 5-DMBz: Fig. 9).

5. Database survey

A search in the Cambridge Structural Database (Version 5.39, update February 2018, Groom et al., 2016) for dimethoxybenzaldehydes derivatives yielded the crystal structure of 93 compounds, which can be subdivided into fourteen 2,3-DMBz derivatives (including two solvates), fifteen 2,4-DMBz derivatives (including four solvates), ten 2,5-DMBz derivatives (including two solvates), nine 2,6-DMBz derivatives (including one solvate), forty two 3,4-DMBz derivatives (including nine solvates) and three 3,5-DMBz derivatives.
Table 3
Experimental details.

|                  | 2,3DMBz | 2,4DMBz | 2,5DMBz | 3,5DMBz |
|------------------|---------|---------|---------|---------|
| Crystal data     |         |         |         |         |
| Chemical formula | C9H10O3 | C9H10O3 | C9H10O3 | C9H10O3 |
| Mr               | 166.17  | 166.17  | 166.17  | 166.17  |
| Crystal system, space group | Monoclinic, P21/c | Monoclinic, P21/c | Monoclinic, P21/n | Monoclinic, P21/c |
| Temperature (K)  | 150     | 150     | 150     | 110.762 (5) |
| a, b, c (Å)      | 7.6152 (3), 15.5513 (6), 7.5891 (3) | 15.1575 (8), 3.9638 (2), 14.6181 (8) | 11.7602 (5), 13.8957 (6), 11.4532 (5) |
| β (°)            | 115.8831 (18) | 113.8888 (19) | 118.642 (2) |
| V (Å³)           | 808.59 (6) | 803.35 (7) | 797.66 (10) |
| Z                | 4       | 4       | 4       | 8       |
| m (mm⁻¹)         | 0.10    | 0.10    | 0.10    | 0.10    |
| Crystal size (mm) | 0.49 x 0.45 x 0.16 | 0.50 x 0.43 x 0.40 | 0.74 x 0.38 x 0.13 | 0.50 x 0.43 x 0.40 |

|                  |         |         |         |         |
| Data collection  |         |         |         |         |
| Diffractometer   | Bruker D8 Quest APEX3 | Bruker D8 Quest APEX3 | Bruker D8 Quest APEX3 | Bruker D8 Quest APEX3 |
| Absorption correction | Multi-scan (SADABS; Krause et al., 2015) | Multi-scan (SADABS; Krause et al., 2015) | Multi-scan (SADABS; Krause et al., 2015) | Multi-scan (SADABS; Krause et al., 2015) |
| Tmin, Tmax       | 0.672, 0.747 | 0.685, 0.746 | 0.705, 0.747 | 0.703, 0.747 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 17821, 4126, 3160 | 15236, 2461, 2171 | 30235, 3873, 3276 | 53075, 7976, 6730 |
| Rint             | 0.032   | 0.020   | 0.024   | 0.030   |
| (sin θ/λ)max (Å⁻¹) | 0.849   | 0.714   | 0.834   | 0.836   |
| Refinement       |         |         |         |         |
| R(F² > 2σ(F²)), wR(F²), S | 0.043, 0.130, 1.02 | 0.039, 0.117, 1.03 | 0.039, 0.124, 1.02 | 0.042, 0.126, 1.05 |
| No. of reflections | 4126   | 2461   | 3873   | 7976   |
| No. of parameters | 111    | 111    | 111    | 222    |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| Deρmax, Deρmin (e Å⁻³) | 0.60, −0.24 | 0.40, −0.24 | 0.54, −0.22 | 0.48, −0.26 |

Computer programs: APEX3 and SAINT (Bruker, 2012), PEAKREF (Schreurs, 2013), SHELXTL2014/4 (Sheldrick, 2015a), SHELXL2016/6 (Sheldrick, 2015b), PLATON (Spek, 2009) and ShelXLe (Hübschle et al., 2011).

Figure 8
Powder X-ray diffraction measurements of form I (black) and II (blue) of 3,4-DMBz. The powder pattern (red) was calculated from the crystal structure by de Ronde et al. (2016).

Figure 9
Powder X-ray diffraction measurements of form I (black) and II (blue) of 3,5-DMBz. The powder pattern (red) was calculated from the crystal structure.
6. Synthesis and crystallization

6.1. 2,3-dimethoxybenzaldehyde

30 mg of 2,3-dimethoxybenzaldehyde (97%, Fluorochem) was dissolved in 4 mL of isopropyl ether. Slow evaporation of a 1:1 mixture of this solution and heptane yielded colorless block-shaped crystals suitable for single crystal X-ray diffraction.

6.2. 2,4-dimethoxybenzaldehyde

25 mg of 2,4-dimethoxybenzaldehyde (98%, Aldrich) was dissolved in a 1:1 ratio of heptane/acetone (1.5 mL). Slow evaporation yielded colorless block-shaped crystals suitable for single crystal X-ray diffraction.

6.3. 2,5-dimethoxybenzaldehyde

1 g of 2,5-dimethoxybenzaldehyde (97%, Acros Organics) was dissolved in a mixture of heptane (1 mL) and acetone (1 mL). Slow evaporation yielded colorless needles suitable for single crystal X-ray diffraction.

6.4. 3,5-dimethoxybenzaldehyde

It was noted that 3,5-dimethoxybenzaldehyde (98%, Aldrich) oils out from solution, therefore the same method was used as had previously been employed for 3,4-dimethoxybenzaldehyde (de Ronde et al., 2016). In short, a few crystals of the commercial powder were added to a saturated solution in water. Subsequently, the temperature was cycled between 298 and 303 K. This resulted in the growth of single crystals suitable for single-crystal X-ray diffraction in several weeks.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were positioned geometrically and refined as riding with C—H = 0.95–0.96 and \( U_{iso}(H) = 1.2–1.5U_{eq}(C) \). The crystal of 3,5-DMBz studied was refined as a two-component twin.

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Computing details

For all structures, data collection: APEX3 (Bruker, 2012); cell refinement: PEAKREF (Schreurs, 2013); data reduction: SAINT (Bruker, 2012); program(s) used to solve structure: SHELXT2014/4 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2016/6 (Sheldrick, 2015b); molecular graphics: PLATON (Spek, 2009), ShelXLe (Hübschle et al., 2011).

2,3-Dimethoxybenzaldehyde (23DMBz)

Crystal data

C₉H₈O₃

Mr = 166.17

Monoclinic, P2₁/c

a = 7.6152 (3) Å

b = 15.5513 (6) Å

V = 808.59 (6) Å³

Z = 4

F(000) = 352

Dₐ = 1.365 Mg m⁻³

Melting point: 322 K

Mo Ka radiation, λ = 0.71073 Å

Cell parameters from 6893 reflections

θ = 2.6–36.9°

μ = 0.10 mm⁻¹

T = 150 K

Block, colourless

0.49 × 0.45 × 0.16 mm

Data collection

Bruker D8 Quest APEX3
diffractometer

17821 measured reflections

4126 independent reflections

3160 reflections with I > 2σ(I)

R(int) = 0.032

θ_max = 37.1°, θ_min = 2.6°

h = −12→12

k = −26→26

l = −12→12

Refinement

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.043

wR(F²) = 0.130

S = 1.02

4126 reflections

111 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

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supporting information

\[ w = 1/\left[\sigma^2(F_o^2) + (0.0743P)^2 + 0.0948P\right] \]
where \( P = (F_o^2 + 2F_c^2)/3 \)
\((\Delta/\sigma)_{\text{max}} = 0.001\)

\[ \Delta\rho_{\text{max}} = 0.60 \text{ e } \AA^{-3} \]
\[ \Delta\rho_{\text{min}} = -0.24 \text{ e } \AA^{-3} \]

**Special details**

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

|     | x        | y        | z        | Uiso*/Ueq |
|-----|----------|----------|----------|-----------|
| O01 | 0.84423  | 0.67610  | 0.72112  | 0.01819 (11) |
| O02 | 0.93597  | 0.50880  | 0.76827  | 0.02194 (12) |
| O03 | 0.42554  | 0.77393  | 0.22027  | 0.03084 (15) |
| C04 | 0.60779  | 0.65162  | 0.38944  | 0.01633 (12) |
| C05 | 0.79724  | 0.53265  | 0.58899  | 0.01586 (12) |
| C06 | 0.50903  | 0.59449  | 0.23432  | 0.02083 (14) |
| H07 | 0.41097  | 0.61517  | 0.113675 | 0.025* |
| C07 | 0.75191  | 0.62098  | 0.56613  | 0.01466 (12) |
| C08 | 0.55760  | 0.74397  | 0.36618  | 0.02121 (14) |
| H08 | 0.632072 | 0.781899 | 0.470279 | 0.025* |
| C09 | 0.69865  | 0.47667  | 0.43414  | 0.01968 (13) |
| H09 | 0.729027 | 0.417067 | 0.448365 | 0.024* |
| C10 | 0.55498  | 0.50806  | 0.25774  | 0.02239 (15) |
| H10 | 0.487993 | 0.469473 | 0.152498 | 0.027* |
| C11 | 1.04331  | 0.69266  | 0.75867  | 0.02355 (15) |
| H11A| 1.113534 | 0.638043 | 0.778082 | 0.035* |
| H11B| 1.106109 | 0.728092 | 0.876679 | 0.035* |
| H11C| 1.045946 | 0.723144 | 0.646820 | 0.035* |
| C12 | 0.98881  | 0.41998  | 0.79585  | 0.02495 (16) |
| H12A| 0.872738 | 0.385147 | 0.769517 | 0.037* |
| H12B| 1.086092 | 0.410593 | 0.931161 | 0.037* |
| H12C| 1.043851 | 0.403253 | 0.705808 | 0.037* |

**Atomic displacement parameters (Å²)**

|     | U₁₁     | U₂₂     | U₃₃     | U₁₂     | U₁₃     | U₂₃     |
|-----|---------|---------|---------|---------|---------|---------|
| O01 | 0.0179  | 0.0172  | 0.0179  | -0.00017 | 0.00634 | -0.00429 |
| O02 | 0.0282  | 0.0151  | 0.0174  | 0.00471  | 0.0052  | 0.00247  |
| O03 | 0.0228  | 0.0306  | 0.0343  | 0.0108   | 0.0081  | 0.0124   |
| C04 | 0.0142  | 0.0176  | 0.0168  | 0.0012   | 0.0064  | 0.0019   |
| C05 | 0.0180  | 0.0140  | 0.0157  | 0.0007   | 0.0075  | 0.0007   |
| C06 | 0.0171  | 0.0265  | 0.0164  | -0.0016  | 0.0049  | -0.0001  |
| C07 | 0.0147  | 0.0138  | 0.0153  | 0.0003   | 0.0064  | -0.00084 |
| C08 | 0.0185  | 0.0207  | 0.0250  | 0.0049   | 0.0100  | 0.0050   |
| C09 | 0.0240  | 0.0156  | 0.0207  | -0.0029  | 0.0110  | -0.0034  |
| C10 | 0.0229  | 0.0240  | 0.0189  | -0.0061  | 0.0078  | -0.0057  |

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|    | 0.0193 (3) | 0.0225 (3) | 0.0254 (3) | −0.0045 (3) | 0.0067 (3) | −0.0055 (3) |
|----|------------|------------|------------|-----------|----------|-----------|
| C12| 0.0324 (4) | 0.0170 (3) | 0.0272 (3) | 0.0085 (3) | 0.0147 (3) | 0.0064 (3) |

**Geometric parameters (Å, °)**

| Bond/Angle | Length/Distance | C06—H06 | C08—H08 | C09—C10 | C10—H10 | C11—H11A | C11—H11B | C11—H11C |
|------------|----------------|---------|---------|---------|---------|----------|----------|----------|
| O01—C07    | 1.3750 (8)     |         |         |         |         |          |          |          |
| O01—C11    | 1.4383 (10)    |         |         |         |         |          |          |          |
| O02—C05    | 1.3601 (9)     | C09—C10|         |         |         |          |          |          |
| O02—C12    | 1.4284 (9)     |         |         |         |         |          |          |          |
| O03—C08    | 1.2175 (9)     | C10—H10|         |         |         |          |          |          |
| C04—C07    | 1.3945 (9)     | C11—H11A|        |         |         |          |          |          |
| C04—C06    | 1.4029 (10)    | C11—H11B|        |         |         |          |          |          |
| C04—C08    | 1.4767 (10)    | C11—H11C|        |         |         |          |          |          |
| C05—C09    | 1.3901 (10)    | C12—H12A|        |         |         |          |          |          |
| C05—C07    | 1.4085 (9)     | C12—H12B|        |         |         |          |          |          |
| C06—C10    | 1.3807 (12)    | C12—H12C|        |         |         |          |          |          |

| Bond/Angle | Length/Distance | C05—C09| H09     | C10—C09| H09     | C05—C11| H11A    | C11—H11B|
|------------|----------------|--------|---------|--------|---------|--------|---------|----------|
| C07—O01—C11| 112.47 (6)    | C05—C09—H09| 120.0  | C10—C09—H09| 120.0  |        |          |          |
| C05—O02—C12| 117.16 (6)    | C10—C09—H09| 120.0  |        |          |          |          |          |
| C07—C04—C06| 119.94 (7)    | C06—C10—C09| 120.82 (7)|        |          |          |          |          |
| C07—C04—C08| 120.08 (6)    | C06—C10—H10| 119.6  |        |          |          |          |          |
| C06—C04—C08| 119.98 (6)    | C09—C10—H10| 119.6  |        |          |          |          |          |
| O02—C05—C09| 124.88 (6)    | O01—C11—C11A| 109.5  |        |          |          |          |          |
| O02—C05—C07| 115.51 (6)    | O01—C11—C11B| 109.5  |        |          |          |          |          |
| C09—C05—C07| 119.59 (6)    | H11A—C11—C11B| 109.5  |        |          |          |          |          |
| C10—C06—C04| 119.71 (7)    | O01—C11—H11C| 109.5  |        |          |          |          |          |
| C10—C06—H06| 120.1        | H11A—C11—H11C| 109.5  |        |          |          |          |          |
| C04—C06—H06| 120.1        | H11B—C11—H11C| 109.5  |        |          |          |          |          |
| O01—C07—C04| 120.23 (6)    | O02—C12—H12A| 109.5  |        |          |          |          |          |
| O01—C07—C05| 119.76 (6)    | O02—C12—H12B| 109.5  |        |          |          |          |          |
| C04—C07—C05| 119.96 (6)    | H12A—C12—H12B| 109.5  |        |          |          |          |          |
| O03—C08—C04| 123.28 (8)    | O02—C12—H12C| 109.5  |        |          |          |          |          |
| O03—C08—H08| 118.4        | H12A—C12—H12C| 109.5  |        |          |          |          |          |
| C04—C08—H08| 118.4        | H12B—C12—H12C| 109.5  |        |          |          |          |          |
| C05—C09—C10| 119.98 (7)    |        |          |        |          |          |          |          |

| Bond/Angle | Length/Distance | O02—C05—O01| C09—C05—O01| C07—O01| C07—O01|
|------------|----------------|------------|------------|--------|--------|
| C12—O02—C05—C09| 2.55 (11) | O02—C05—C07—O01| 178.73 (6)|        |        |
| C12—O02—C05—C07| −178.75 (6)| C09—C05—C07—O01| 178.31 (7)|        |        |
| C07—C04—C06—C10| 0.13 (11) | O02—C05—C07—C04| −178.28 (6)|        |        |
| C08—C04—C06—C10| −179.23 (7)| C09—C05—C07—C04| 0.51 (10) |        |        |
| C11—O01—C07—C04| −108.70 (7)| C07—C04—C08—O03| −175.45 (7)|        |        |
| C11—O01—C07—C05| 74.09 (8) | C06—C04—C08—O03| 3.90 (11) |        |        |
| C06—C04—C07—O01| −177.61 (6)| O02—C05—C09—C10| 178.31 (7)|        |        |
| C08—C04—C07—O01| 1.75 (10) | C07—C05—C09—C10| −0.34 (11) |        |        |
| C06—C04—C07—C05| −0.40 (10) | C04—C06—C10—C09| 0.03 (11) |        |        |
| C08—C04—C07—C05| 178.96 (6) | C05—C09—C10—C06| 0.08 (11) |        |        |
2,4-Dimethoxybenzaldehyde (24DMBz)

Crystal data

C₉H₁₀O₃  
Mr = 166.17  
Monoclinic, P2₁/c  

a = 15.1575 (8) Å  
b = 3.9638 (2) Å  
c = 14.6181 (8) Å  
β = 113.8388 (19)°  
V = 803.35 (7) Å³  
Z = 4  

F(000) = 352  
Dx = 1.374 Mg m⁻³  
Melting point: 341 K  

Data collection

Bruker D8 Quest APEX3  
Radiation source: sealed tube  
Graphite monochromator  
Detector resolution: 10.4 pixels mm⁻¹  
φ and ω scans  
Absorption correction: multi-scan  
(SADABS; Krause et al., 2015)  

15236 measured reflections  
2461 independent reflections  
2171 reflections with I > 2σ(I)  
Rint = 0.020  
θmax = 30.5°, θmin = 2.8°  
h = −21→21  
k = −5→5  
l = −20→19

Refinement

Refinement on F²  
Least-squares matrix: full  

R[F² > 2σ(F²)] = 0.039  
wR(F²) = 0.117  
S = 1.03  

2461 reflections  
111 parameters  
0 restraints  

Secondary atom site location: difference Fourier map  
Hydrogen site location: inferred from neighbouring sites  
H-atom parameters constrained

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|    | x       | y       | z       | Ueq     |
|----|---------|---------|---------|---------|
| O01| 0.08102 (5) | 0.65429 (18) | 0.10801 (5) | 0.02325 (16) |
| O02| 0.39771 (5) | 0.76391 (19) | 0.37610 (5) | 0.02571 (17) |
| O03| 0.31680 (6) | 0.2357 (2) | 0.56154 (5) | 0.0358 (2) |
| C04| 0.30419 (6) | 0.6579 (2) | 0.33618 (6) | 0.01822 (17) |
| C05| 0.27290 (6) | 0.4771 (2) | 0.40045 (6) | 0.01952 (18) |
| C06| 0.14709 (6) | 0.6063 (2) | 0.20292 (6) | 0.01766 (17) |
| C07| 0.24207 (6) | 0.7210 (2) | 0.23720 (6) | 0.01809 (17) |

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|          | \( u_{11} \) | \( u_{22} \) | \( u_{33} \) | \( u_{12} \) | \( u_{13} \) | \( u_{23} \) |
|----------|---------------|---------------|---------------|---------------|---------------|---------------|
| O01      | 0.0204 (3)    | 0.0285 (3)    | 0.0187 (3)    | -0.0020 (2)   | 0.0057 (2)    | 0.0016 (2)    |
| O02      | 0.0180 (3)    | 0.0327 (4)    | 0.0249 (3)    | -0.0049 (3)   | 0.0071 (2)    | 0.0042 (3)    |
| O03      | 0.0340 (4)    | 0.0489 (5)    | 0.0239 (3)    | -0.0020 (3)   | 0.0111 (3)    | 0.0108 (3)    |
| C04      | 0.0169 (3)    | 0.0182 (4)    | 0.0204 (4)    | 0.0001 (3)    | 0.0084 (3)    | -0.0010 (3)   |
| C05      | 0.0211 (4)    | 0.0201 (4)    | 0.0186 (4)    | 0.0008 (3)    | 0.0093 (3)    | 0.0001 (3)    |
| C06      | 0.0189 (4)    | 0.0163 (3)    | 0.0181 (3)    | 0.0013 (3)    | 0.0077 (3)    | -0.0022 (3)   |
| C07      | 0.0194 (4)    | 0.0176 (3)    | 0.0194 (4)    | 0.0003 (3)    | 0.0100 (3)    | -0.0001 (3)   |
| C08      | 0.0191 (4)    | 0.0194 (4)    | 0.0229 (4)    | -0.0016 (3)   | 0.0106 (3)    | -0.0018 (3)   |
| C09      | 0.0229 (4)    | 0.0198 (4)    | 0.0218 (4)    | -0.0003 (3)   | 0.0131 (3)    | 0.0000 (3)    |
| C10      | 0.0269 (4)    | 0.0249 (4)    | 0.0188 (4)    | -0.0002 (3)   | 0.0092 (3)    | 0.0011 (3)    |
| C11      | 0.0251 (4)    | 0.0335 (5)    | 0.0215 (4)    | -0.0011 (4)   | 0.0078 (3)    | 0.0034 (3)    |
| C12      | 0.0215 (4)    | 0.0296 (5)    | 0.0337 (5)    | -0.0017 (3)   | 0.0134 (4)    | 0.0068 (4)    |

Geometric parameters (Å, °)

|          | C06   | C07   | C08   | C09   | C10   | C11   | C12   | C13   | C14   | C15   | C16   | C17   | C18   | C19   | C20   |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| O01—C06  | 1.3567 (10) | C07—H07 | 0.9500 |       |       |       |       |       |       |       |       |       |       |       |       |
| O01—C10  | 1.4347 (11) | C08—C09 | 1.3756 (12) |       |       |       |       |       |       |       |       |       |       |       |       |
| O02—C04  | 1.3629 (10) | C08—H08 | 0.9500 |       |       |       |       |       |       |       |       |       |       |       |       |
| O02—C12  | 1.4326 (11) | C09—H09 | 0.9500 |       |       |       |       |       |       |       |       |       |       |       |       |
| O03—C11  | 1.2201 (12) | C10—H10A | 0.9800 |       |       |       |       |       |       |       |       |       |       |       |       |
| C04—C07  | 1.3934 (11) | C10—H10B | 0.9800 |       |       |       |       |       |       |       |       |       |       |       |       |
| C04—C05  | 1.4077 (11) | C10—H10C | 0.9800 |       |       |       |       |       |       |       |       |       |       |       |       |
| C05—C09  | 1.4057 (12) | C11—H11 | 0.9500 |       |       |       |       |       |       |       |       |       |       |       |       |
| C05—C11  | 1.4608 (12) | C12—H12A | 0.9800 |       |       |       |       |       |       |       |       |       |       |       |       |
| C06—C07  | 1.3954 (11) | C12—H12B | 0.9800 |       |       |       |       |       |       |       |       |       |       |       |       |
| C06—C08  | 1.4007 (11) | C12—H12C | 0.9800 |       |       |       |       |       |       |       |       |       |       |       |       |
O02—C04—C07  122.59 (7)  O01—C10—H10A  109.5
O02—C04—C05  116.35 (7)  O01—C10—H10B  109.5
C07—C04—C05  121.05 (7)  H10A—C10—H10B  109.5
C09—C05—C04  118.29 (7)  O01—C10—H10C  109.5
C09—C05—C11  120.43 (8)  H10B—C10—H10C  109.5
C04—C05—C11  121.24 (8)  O01—C06—C07  123.34 (8)  O03—C11—C05  124.40 (9)
C01—C06—C07  115.29 (7)  O03—C11—H11  117.8
C07—C06—C08  121.37 (8)  C05—C11—H11  117.8
C04—C07—C06  118.72 (8)  O02—C12—H12A  109.5
C04—C07—H07  120.6  O02—C12—H12B  109.5
C06—C07—H07  120.6  H12A—C12—H12B  109.5
C09—C08—C06  120.5  H12A—C12—H12C  109.5
C09—C08—H08  120.5  C05—C09—C08  121.24 (8)
C06—C08—H08  120.5  O02—C12—H12C  109.5
C08—C09—C05  121.60 (8)  C12—O02—C04—C07 −4.23 (12)  O01—C06—C07—C04 −179.94 (7)
C12—O02—C04—C05  175.40 (8)  C08—C06—C07—C04 −0.36 (12)  C12—O02—C04—C05  175.40 (8)
O02—C04—C05—C09 −0.88 (13)  C07—C06—C08—C09 −0.60 (12)  O02—C04—C05—C09 −2.82 (13)
O02—C04—C05—C11 −2.82 (13)  C06—C08—C09—C05  0.83 (13)  C07—C04—C05—C11 −0.88 (13)
C07—C04—C05—C11  176.82 (8)  C04—C05—C09—C08 −0.11 (13)
C10—O01—C06—C07  4.17 (12)  O01—C06—C08—C09 −177.83 (8)
C10—O01—C06—C08 −175.43 (7)  C11—C05—C09—C08  4.17 (12)
C10—O01—C06—C09 −179.28 (8)  C11—C05—C09—C08 −177.83 (8)
C02—C04—C07—C06 −179.28 (8)  C04—C05—C11—O03  1.10 (12)
C02—C04—C07—C08 −175.43 (7)  C09—C05—C11—O03 −1.27 (16)
C02—C04—C07—C09 −179.28 (8)  C04—C05—C11—O03 −178.93 (10)
C02—C04—C07—C10  1.10 (12)

2,5-Dimethoxybenzaldehyde (25DMBz)

Crystal data
$\text{C}_9\text{H}_{10}\text{O}_3$

$M_r = 166.17$

Monoclinic, $P2_1/n$

$a = 3.8780$ (3) $\text{Å}$

$b = 11.5513$ (7) $\text{Å}$

$c = 17.8153$ (12) $\text{Å}$

$\beta = 91.808$ (2)$^\circ$

$V = 797.66$ (10) $\text{Å}^3$

$Z = 4$

$F(000) = 352$

$D_r = 1.384$ Mg m$^{-3}$

Melting point: 321 K

$\text{Mo } K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9955 reflections

$\theta = 2.3$–$36.2^\circ$

$\mu = 0.10$ mm$^{-1}$

$T = 150$ K

Needle, colourless

$0.74 \times 0.38 \times 0.13$ mm

Data collection

Bruker D8 Quest APEX3
diffractometer

30235 measured reflections

3873 independent reflections

3276 reflections with $I > 2\sigma(I)$

$R_{int} = 0.024$

$\theta_{max} = 36.4^\circ$, $\theta_{min} = 2.1^\circ$

$h = -6$–$6$

$k = -14$–$19$

$l = -29$–$29$

$(\text{SADABS}; \text{Krause et al., 2015})$

$T_{min} = 0.705$, $T_{max} = 0.747$
Refinement

Refinement on \( F^2 \)  
Least-squares matrix: full  
\( R[F^2 > 2\sigma(F^2)] = 0.039 \)  
\( wR(F^2) = 0.124 \)  
\( S = 1.02 \)  
3873 reflections  
111 parameters  
0 restraints

Primary atom site location: structure-invariant direct methods  
Secondary atom site location: difference Fourier map  
Hydrogen site location: inferred from neighbouring sites  
H-atom parameters constrained

\( w = 1/[\sigma^2(F_o^2) + (0.0691P)^2 + 0.1755P] \)  
\( (\Delta/\sigma)_{\text{max}} = 0.001 \)  
\( \Delta \rho_{\text{max}} = 0.54 \, \text{e} \, \text{Å}^{-3} \)  
\( \Delta \rho_{\text{min}} = -0.22 \, \text{e} \, \text{Å}^{-3} \)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|     | x          | y          | z          | U(eq)  
|-----|------------|------------|------------|--------
| O01 | 0.70027 (15) | 0.37815 (5) | 0.56706 (3) | 0.02308 (11) |
| O02 | 0.32551 (16) | 0.55079 (5) | 0.84287 (3) | 0.02348 (12) |
| O03 | 0.81653 (19) | 0.71583 (5) | 0.60790 (3) | 0.02970 (14) |
| C04 | 0.64196 (16) | 0.53211 (5) | 0.65291 (3) | 0.01623 (11) |
| C05 | 0.54777 (16) | 0.57451 (5) | 0.72267 (3) | 0.01719 (11) |
| H05 | 0.580616 | 0.654118 | 0.734217 | 0.021* |
| C06 | 0.44894 (18) | 0.34122 (6) | 0.68849 (4) | 0.01849 (12) |
| H06 | 0.413247 | 0.261704 | 0.677056 | 0.022* |
| C07 | 0.40630 (16) | 0.50128 (5) | 0.77542 (3) | 0.01656 (11) |
| C08 | 0.35490 (17) | 0.38467 (6) | 0.75789 (4) | 0.01814 (12) |
| H08 | 0.255150 | 0.334576 | 0.793501 | 0.022* |
| C09 | 0.59531 (16) | 0.41403 (5) | 0.65371 (3) | 0.01655 (11) |
| C10 | 0.79366 (19) | 0.61160 (6) | 0.59830 (4) | 0.02189 (13) |
| H10 | 0.878085 | 0.579933 | 0.553220 | 0.026* |
| C11 | 0.6662 (2) | 0.25766 (6) | 0.55053 (4) | 0.02393 (14) |
| H11A | 0.787349 | 0.212440 | 0.589721 | 0.036* |
| H11B | 0.766517 | 0.241337 | 0.501841 | 0.036* |
| H11C | 0.421362 | 0.236493 | 0.548665 | 0.036* |
| C12 | 0.1987 (2) | 0.47519 (7) | 0.89872 (4) | 0.02583 (15) |
| H12A | -0.020111 | 0.441090 | 0.880789 | 0.039* |
| H12B | 0.161901 | 0.518945 | 0.944911 | 0.039* |
| H12C | 0.367146 | 0.413466 | 0.908934 | 0.039* |

Atomic displacement parameters (Å²)

|     | U^11 | U^22 | U^33 | U^12 | U^13 | U^23 |
|-----|------|------|------|------|------|------|
| O01 | 0.0330 (3) | 0.0181 (2) | 0.0185 (2) | -0.00401 (19) | 0.00611 (18) | -0.00154 (16) |
| O02 | 0.0348 (3) | 0.0174 (2) | 0.0187 (2) | 0.00073 (19) | 0.00818 (19) | 0.00082 (16) |
| O03 | 0.0450 (3) | 0.0186 (2) | 0.0256 (3) | -0.0097 (2) | 0.0032 (2) | 0.00350 (18) |
C04 0.0178 (2) 0.0145 (2) 0.0164 (2) −0.00141 (18) 0.00017 (18) 0.00262 (18)
C05 0.0197 (2) 0.0141 (2) 0.0178 (2) −0.00057 (19) 0.00054 (19) 0.00188 (19)
C06 0.0222 (3) 0.0146 (2) 0.0186 (2) −0.00275 (19) 0.0011 (2) 0.00149 (19)
C07 0.0179 (2) 0.0156 (2) 0.0163 (2) 0.00086 (19) 0.00157 (18) 0.00161 (18)
C08 0.0205 (3) 0.0158 (2) 0.0183 (2) −0.00184 (19) 0.00202 (19) 0.00261 (18)
C09 0.0182 (2) 0.0155 (2) 0.0160 (2) −0.00112 (19) 0.00054 (19) 0.00083 (18)
C10 0.0277 (3) 0.0191 (3) 0.0189 (3) −0.0051 (2) 0.0018 (2) 0.0032 (2)
C11 0.0306 (3) 0.0194 (3) 0.0219 (3) −0.0011 (2) 0.0020 (2) −0.0034 (2)
C12 0.0322 (4) 0.0232 (3) 0.0227 (3) 0.0033 (3) 0.0109 (3) 0.0042 (2)

Geometric parameters (Å, °)

O01—C09 1.3655 (8) C06—C09 1.3954 (9) O01—C09—C04 116.67 (5)
O01—C11 1.4280 (9) C06—H06 0.9500
O02—C07 1.3757 (8) C07—C08 1.3957 (9) O02—C12—H12A 109.5
O02—C12 1.4232 (9) C08—H08 0.9500
O03—C10 1.2189 (9) C10—H10 0.9500
C04—C05 1.3952 (9) C11—H11A 0.9800
C04—C09 1.4083 (9) C11—H11B 0.9800
C04—C10 1.4738 (9) C11—H11C 0.9800
C05—C07 1.3901 (9) C12—H12A 0.9800
C05—H05 0.9500 C12—H12B 0.9800
C06—C08 1.3936 (9) C12—H12C 0.9800
C09—C01—C11 116.90 (5) O01—C09—C04 116.67 (5)
C07—O02—C07 116.67 (6) C06—C09—C04 119.30 (6)
C05—C04—C09 119.89 (6) O03—C10—C04 123.47 (7)
C05—C04—C10 119.37 (6) O03—C10—H10 118.3
C09—C04—C10 120.73 (6) C04—C10—H10 118.3
C07—C05—C04 120.57 (6) O01—C11—H11A 109.5
C07—C05—H05 119.7 O01—C11—H11B 109.5
C04—C05—C04 119.7 O01—C11—H11C 109.5
C08—C06—C09 120.27 (6) O01—C11—H11D 109.5
C08—C06—H06 119.9 H11A—C11—H11B 109.5
C09—C06—H06 119.9 H11A—C11—H11C 109.5
O02—C07—C05 116.31 (6) H11B—C11—H11C 109.5
O02—C07—C08 124.18 (6) O02—C12—H12A 109.5
C05—C07—C08 119.51 (6) O02—C12—H12B 109.5
C06—C08—C07 120.44 (6) O02—C12—H12C 109.5
C06—C08—H08 119.8 H12A—C12—H12B 109.5
C07—C08—H08 119.8 H12A—C12—H12C 109.5
C01—O01—C09 116.90 (5) O01—C09—C04 116.67 (5)
C04—C05—C07 −0.32 (9) C11—O01—C09—C04 177.58 (6)
C04—C05—C07 −179.56 (6) C08—C06—C09—O01 178.78 (6)
C12—O02—C07—C05 −176.57 (6) C08—C06—C09—C04 −0.97 (10)
C12—O02—C07—C08 3.41 (10) C05—C04—C09—O01 −178.60 (6)
C04—C05—C07—O02 179.25 (6) C10—C04—C09—O01 0.63 (9)
3,5-Dimethoxybenzaldehyde (35DMBz)

Crystal data

\[ \text{C}_9\text{H}_{10}\text{O}_3 \]

\[ M_r = 166.17 \]

Monoclinic, \( P\overline{2}_1/c \)

\[ a = 11.7602 (5) \text{ Å} \]

\[ b = 13.8957 (6) \text{ Å} \]

\[ c = 11.4352 (5) \text{ Å} \]

\[ \beta = 118.642 (2)° \]

\[ V = 1640.03 (13) \text{ Å}^3 \]

\[ Z = 8 \]

\[ F(000) = 704 \]

Melting point: 319 K

Mo \( K\alpha \) radiation, \( \lambda = 0.71073 \text{ Å} \)

Cell parameters from 9794 reflections

\[ \theta = 2.5–36.4° \]

\[ \mu = 0.10 \text{ mm}^{-1} \]

\[ T = 150 \text{ K} \]

Block, colourless

\[ 0.50 \times 0.43 \times 0.40 \text{ mm} \]

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\[ R(F^2 > 2\sigma(F^2)) = 0.042 \]

\[ wR(F) = 0.126 \]

\[ S = 1.05 \]

7976 reflections

222 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

Secondary atom site location: difference Fourier map

\[ \Delta \rho_{\text{max}} = 0.48 \text{ e Å}^{-3} \]

\[ \Delta \rho_{\text{min}} = -0.25 \text{ e Å}^{-3} \]

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a two-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å\(^2\))

|           | \( x \)       | \( y \)       | \( z \)       | \( U_{eq} \) |
|-----------|---------------|---------------|---------------|-------------|
| O01       | 0.10858 (7)   | 0.50152 (5)   | 0.16802 (7)   | 0.02241 (12) |
| Atomic displacement parameters (Å²) |
|-----------------------------------|
| O01  | 0.0291 (3) | 0.0174 (3) | 0.0313 (3) | −0.0012 (2) | 0.0229 (3) | −0.0018 (2) |

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### Geometric parameters (Å, °)

| Bond                  | Distance (Å) | Angle (°) |
|-----------------------|--------------|-----------|
| O01—C09               | 1.3594 (10)  | C13—C19 1.4014 (11) |
| O01—C24               | 1.4297 (11)  | C13—H13 0.9500 |
| O02—C20               | 1.2144 (10)  | C14—H14 0.9500 |
| O03—C12               | 1.3624 (10)  | C15—C16 1.4000 (10) |
| O03—C21               | 1.4292 (11)  | C16—H16 0.9500 |
| O04—C10               | 1.3609 (10)  | C17—C19 1.4797 (12) |
| O04—C22               | 1.4321 (11)  | C17—H17 0.9500 |
| O05—C15               | 1.3623 (9)   | C18—C19 1.3898 (11) |
| O05—C23               | 1.4275 (10)  | C18—H18 0.9500 |
| O06—C17               | 1.2120 (12)  | C20—H20 0.9500 |
| C07—C09               | 1.3918 (11)  | C21—H21A 0.9800 |
| C07—C12               | 1.4025 (11)  | C21—H21B 0.9800 |
| C07—H07               | 0.9500       | C21—H21C 0.9800 |
| C08—C12               | 1.3923 (11)  | C22—H22A 0.9800 |
| C08—C11               | 1.4003 (11)  | C22—H22B 0.9800 |
| C08—H08               | 0.9500       | C22—H22C 0.9800 |
| C09—C14               | 1.4014 (11)  | C23—H23A 0.9800 |
| C10—C16               | 1.3914 (11)  | C23—H23B 0.9800 |
| C10—C18               | 1.3996 (11)  | C23—H23C 0.9800 |
| C11—C14               | 1.3884 (11)  | C24—H24A 0.9800 |
| C11—C20               | 1.4795 (11)  | C24—H24B 0.9800 |
| C13—C15               | 1.3922 (11)  | C24—H24C 0.9800 |
| Bond                        | Angle (°) (E) | Bond                        | Angle (°) (E) |
|-----------------------------|---------------|-----------------------------|---------------|
| C09—O01—C24                | 117.83 (7)    | O06—C17—H17                | 117.6         |
| C12—O03—C21                | 116.74 (7)    | C19—C17—H17                | 117.6         |
| C10—O04—C22                | 117.72 (7)    | C19—C18—C10                | 118.77 (7)    |
| C15—O05—C23                | 116.88 (6)    | C19—C18—H18                | 120.6         |
| C09—C07—C12                | 119.48 (7)    | C10—C18—H18                | 120.6         |
| C09—C07—H07                | 120.3         | C18—C19—C13                | 121.69 (7)    |
| C12—C08—C11                | 118.39 (7)    | C18—C19—C17                | 119.99 (7)    |
| C12—C08—H08                | 120.8         | C13—C19—C17                | 118.32 (7)    |
| C11—C08—H08                | 120.8         | O02—C20—C11                | 124.56 (8)    |
| O01—C09—C07                | 123.95 (7)    | C11—C20—H20                | 117.7         |
| O01—C09—C14                | 115.37 (7)    | O03—C21—H21A               | 109.5         |
| C07—C09—C14                | 120.68 (7)    | O03—C21—H21B               | 109.5         |
| O04—C10—C16                | 123.58 (7)    | H21A—C21—H21B              | 109.5         |
| O04—C10—C18                | 115.74 (7)    | O03—C21—H21C               | 109.5         |
| C16—C10—C18                | 120.68 (7)    | H21A—C21—H21C              | 109.5         |
| C14—C11—C08                | 121.94 (7)    | H21B—C21—H21C              | 109.5         |
| C14—C11—C20                | 120.39 (7)    | O04—C22—H22A               | 109.5         |
| C08—C11—C20                | 117.66 (7)    | O04—C22—H22B               | 109.5         |
| O03—C12—C08                | 124.06 (7)    | H22A—C22—H22B              | 109.5         |
| O03—C12—C07                | 115.08 (7)    | O04—C22—H22C               | 109.5         |
| C08—C12—C07                | 120.86 (7)    | H22A—C22—H22C              | 109.5         |
| C15—C13—C19                | 118.47 (7)    | H22B—C22—H22C              | 109.5         |
| C15—C13—H13                | 120.8         | O05—C23—H23A               | 109.5         |
| C19—C13—H13                | 120.8         | O05—C23—H23B               | 109.5         |
| C11—C14—C09                | 118.66 (7)    | H23A—C23—H23B              | 109.5         |
| C11—C14—H14                | 120.7         | O05—C23—H23C               | 109.5         |
| C09—C14—H14                | 120.7         | H23A—C23—H23C              | 109.5         |
| O05—C15—C13                | 124.69 (7)    | H23B—C23—H23C              | 109.5         |
| O05—C15—C16                | 114.44 (7)    | O01—C24—H24A               | 109.5         |
| C13—C15—C16                | 120.86 (7)    | O01—C24—H24B               | 109.5         |
| C10—C16—C15                | 119.52 (7)    | H24A—C24—H24B              | 109.5         |
| C10—C16—H16                | 120.2         | O01—C24—H24C               | 109.5         |
| C15—C16—H16                | 120.2         | H24A—C24—H24C              | 109.5         |
| O06—C17—C19                | 124.76 (9)    | H24B—C24—H24C              | 109.5         |
| C24—O01—C09—C07            | 3.19 (13)     | C23—O05—C15—C13            | 3.63 (12)     |
| C24—O01—C09—C14            | −176.62 (8)   | C23—O05—C15—C16            | −176.23 (7)   |
| C12—C07—C09—O01            | −179.69 (7)   | C19—C13—C15—O05            | −179.27 (8)   |
| C12—C07—C09—C14            | 0.11 (12)     | C19—C13—C15—C16            | 0.58 (12)     |
| C22—O04—C10—C16            | −10.72 (12)   | O04—C10—C16—C15            | 179.72 (7)    |
| C22—O04—C10—C18            | 169.48 (8)    | C18—C10—C16—C15            | −0.50 (12)    |
| C12—C08—C11—C14            | −0.02 (11)    | O05—C15—C16—C10            | 179.48 (7)    |
| C12—C08—C11—C20            | 178.95 (7)    | C13—C15—C16—C10            | −0.38 (12)    |
| C21—O03—C12—C08            | 0.13 (12)     | O04—C10—C18—C19            | −179.06 (7)   |
| C21—O03—C12—C07            | 179.77 (8)    | C16—C10—C18—C19            | 1.13 (12)     |
| C11—C08—C12—O03            | 179.42 (7)    | C10—C18—C19—C13            | −0.93 (12)    |
| Bond                  | Dihedral Angle (°) |Bond                  | Dihedral Angle (°) |
|----------------------|--------------------|----------------------|--------------------|
| C11—C08—C12—C07     | 178.64 (8)         | C10—C18—C19—C17     | 0.20 (11)          |
| C09—C07—C12—O03     | 179.50 (7)         | C15—C13—C19—C18     | 0.09 (12)          |
| C09—C07—C12—C08     | 0.15 (12)          | C15—C13—C19—C17     | −179.49 (8)        |
| C08—C11—C14—C09     | 0.28 (11)          | O06—C17—C19—C18     | 4.47 (15)          |
| C20—C11—C14—C09     | −178.66 (7)        | O06—C17—C19—C13     | −175.94 (10)       |
| O01—C09—C14—C11     | 179.50 (7)         | C14—C11—C20—O02     | −1.69 (13)         |
| C07—C09—C14—C11     | −0.32 (12)         | C08—C11—C20—O02     | 179.33 (8)         |