While endeavoring to synthesize new chlorinated ligands for ruthenium-based metathesis catalysts, the title compound, dimethyl 4,5-dichlorophthalate, was prepared from commercially available 4,5-dichlorophthalic acid in ~77% yield. The title molecule, which also finds utility as a precursor molecule for the synthesis of drugs used in the treatment of Alzheimer’s disease, shows one carbonyl-containing methyl ester moiety lying nearly co-planar with the chlorine-derivatized aromatic ring while the second methyl ester shows a significant deviation of 101.05 (12)° from the least-squares plane of the aromatic ring. Within the crystal, structural integrity is maintained by the concerted effects of electrostatic interactions involving the electron-deficient carbonyl carbon atom and the electron-rich aromatic ring along the a-axis direction and C—H⋯O hydrogen bonds between neighboring molecules parallel to b.

Structure description

While endeavoring to synthesize new chlorinated ligands for ruthenium-based metathesis catalysts (Anderson et al., 2006), the title compound, I, was prepared from commercially available 4,5-dichlorophthalic acid in ~77% yield. The title molecule also finds utility as a precursor molecule for the synthesis of drugs used in the treatment of Alzheimer’s disease (Hennessy & Buchwald, 2005).

Compound I crystallizes in the centrosymmetric triclinic space group $P\overline{1}$ with a full molecule of the title compound as the contents of asymmetric unit (Fig. 1, Table 1). Within the structure of I, one of the carbonyl-containing ester groups is nearly co-planar with the aromatic ring demonstrating a deviation of 3.41 (12)° from the least-squares plane of the chlorine-derivatized aromatic ring. The second ester group reveals a much
larger deviation from planarity as the dihedral angle involving the second carbonyl group is 101.05 (12)°.

Looking down the a-axis, and involving a second molecule of I related by inversion, the centroid of the electron-rich, chlorine-derivatized aromatic ring of the first molecule lies above the electron-deficient carbonyl carbon atom of the second at a distance of 3.4600 (12) Å, suggesting the presence of electrostatic interactions (Fig. 2). In addition to the electrostatic interactions, when looking into the bc-plane, between H5 on the aromatic ring and O1 from the carbonyl that is nearly co-planar with the aromatic ring, a C—H⋯O hydrogen bond was observed (Fig. 3, Table 2). A one-dimensional array of symmetry-equivalent molecules of I linked by C—H⋯O hydrogen bonds results along the b-axis direction when looking into the bc-plane (Fig. 3). While there are no additional interactions between neighboring, co-planar one-dimensional arrays parallel to one another along c, weak C—H⋯O [d(C10⋯O3) = 3.54 Å; θ(C10—H10B—O3) = 147°] interactions with a neighboring layer having the symmetry

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

|          | D—H···A | D—H | H···A | D···A | D—H···A |
|----------|----------|------|------|-------|---------|
| C5—H5⋯O1 | 0.95     | 2.33 | 3.2327 (15) | 159 |
| C10—H10B⋯O3 | 0.98 | 2.68 | 3.5380 (16) | 147 |

Symmetry codes: (i) x, y−1, z; (ii) −x+1, −y, −z.

Figure 1
Anisotropic displacement ellipsoid plot of I with ellipsoids set to the 50% probability level.

Figure 2
Solid-state expansion of I showing the superposition of the electron-rich aromatic ring centroid and the electron-deficient carbonyl carbon atom. Anisotropic displacement ellipsoids have been set to the 50% probability level.

Figure 3
Projection of I within the bc-plane showing the C—H⋯O hydrogen bonding between neighboring molecules along b to form one-dimensional arrays. Anisotropic displacement ellipsoids have been set to the 50% probability level. Dashed lines represent hydrogen bonds.

Figure 4
Projection of I within the ac-plane showing the formation of the R21(10) centrosymmetric dimer facilitated by weak C—H⋯O interactions between layers. Anisotropic displacement ellipsoids have been set to the 50% probability level. Dashed lines represent the C—H⋯O interactions.
code \((1-x, -y, -z)\) yielded a centrosymmetric dimer (Fig. 4, Table 2) having the \(R_2^{2}(10)\) graph-set notation (Bernstein et al., 1995).

Synthesis and crystallization

Compound \(1\) was synthesized by adding 4,5-dichlorophthalic acid (23.68 mmol, 5.566 g) to 70 ml of CH\(_3\)OH in a 200 ml flask. While stirring, 1.0 ml H\(_2\)SO\(_4\) (98\%) was added dropwise and the mixture was allowed to reflux at 70\(^\circ\)C overnight. The product was extracted with ethyl acetate, and washed with water, concentrated NaHCO\(_3\), 10\% NaHCO\(_3\), and then a saturated solution of NaCl. After filtering through Na\(_2\)SO\(_4\) to remove trace moisture, the solvent was removed \textit{in vacuo} to yield a clear oil, which later crystallized into small rods. Recrystallization from the mixed solvents of isopropyl alcohol and dichloromethane produced X-ray quality crystals of \(1\) up to 2 mm.

Refinement

Crystal data, data collection and structure refinement details for \(1\) are summarized in Table 2. The choice of the space group \(P\bar{1}\) for \(1\) was unambiguously verified by PLATON (Spek, 2003; Spek, 2020).

Funding information

Funding for this research was provided by: Pomona College; Harvey Mudd College.

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### Table 2

Experimental details.

| Crystal data | Chemical formula | \(C_{10}H_{8}Cl_{2}O_{4}\) |
|--------------|------------------|------------------------|
| Temperature (K) | 173 | |
| \(a, b, c (\text{Å})\) | 7.0204 (6), 7.7661 (6), 10.5392 (8) |
| \(\alpha, \beta, \gamma (^\circ)\) | 97.733 (1), 109.293 (1), 90.217 (1) |
| \(V (\text{Å}^3)\) | 536.69 (7) |
| \(Z\) | 2 |

| Radiation type | Mo Ka |
| \(\mu (\text{mm}^{-1})\) | 0.60 |
| Crystal size (mm) | 0.35 \(\times\) 0.29 \(\times\) 0.28 |

| Data collection | Bruker APEX CCD area detector |
| Absorption correction | Multi-scan (SADABS; Krause et al., 2015) |

| \(T_{\text{min}}, T_{\text{max}}\) | 0.838, 0.927 |
| No. of measured, independent and observed \([I > 2\sigma(I)]\) reflections | 5934, 2582, 2417 |
| \(R_{\text{int}}\) | 0.031 |
| \((\sin \theta/\lambda)_{\text{max}} (\text{Å}^{-1})\) | 0.668 |

| Refinement | \(R(F^2 > 2\sigma(F^2)), wR(F^2), S\) |
| No. of reflections | 2582 |
| No. of parameters | 147 |
| H-atom treatment | H-atom parameters constrained |
| \(\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (\text{e Å}^{-3})\) | 0.45, −0.21 |

Computer programs: APEX2 and SAINT (Bruker, 2016), SHELXT2014/5 (Sheldrick, 2015a), SHELXL2014/7 (Sheldrick, 2015b) and OLEX2 (Dolomanov et al., 2009).
full crystallographic data

IUCrData (2021). 6, x211043  [https://doi.org/10.1107/S2414314621010439]

Dimethyl 4,5-dichlorophthalate

Daniel D. Hickstein, Eric W. Reinheimer, Adam R. Johnson and Daniel J. O’Leary

Dimethyl 4,5-dichlorophthalate

Crystal data

C_{10}H_{8}Cl_{2}O_{4}  
Mr = 263.06  
Triclinic, \( P\bar{1} \)  
\( a = 7.0204 \) (6) Å  
\( b = 7.7661 \) (6) Å  
\( c = 10.5392 \) (8) Å  
\( \alpha = 97.733 \) (1)°  
\( \beta = 109.293 \) (1)°  
\( \gamma = 90.217 \) (1)°  
\( V = 536.69 \) (7) Å\(^3\)  

\( Z = 2 \)  
\( F(000) = 268 \)  
\( D_{r} = 1.628 \) Mg m\(^{-3}\)  
Mo Kα radiation, \( \lambda = 0.71073 \) Å  
Cell parameters from 548 reflections  
\( \theta = 2.4–27.7^\circ \)  
\( \mu = 0.60 \) mm\(^{-1}\)  
\( T = 173 \) K  
Irregular, colorless  
0.35 × 0.29 × 0.28 mm

Data collection

Bruker APEX CCD area detector  
Radiation source: Fine-focus sealed tube  
Graphite monochromator  
phi and \( \omega \) scans  
Absorption correction: multi-scan  
\( (\text{SADABS}; \text{Krause et al.}, 2015) \)  
2417 reflections with \( I > 2\sigma(I) \)  
5934 measured reflections  
2582 independent reflections  
2417 reflections with \( I > 2\sigma(I) \)  
\( T_{\text{min}} = 0.838, T_{\text{max}} = 0.927 \)

Refinement

Refinement on \( F^2 \)  
Least-squares matrix: full  
\( R[F^2 > 2\sigma(F^2)] = 0.026 \)  
\( wR(F^2) = 0.073 \)  
\( S = 1.04 \)  
2582 reflections  
147 parameters  
0 restraints  
Primary atom site location: dual  
Hydrogen site location: inferred from  
neighbouring sites  
H-atom parameters constrained  
\( w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 0.1955P] \)  
where \( P = (F_o^2 + 2F_c^2)/3 \)  
\( \Delta \rho_{\text{max}} = 0.45 \) e Å\(^{-3}\)  
\( \Delta \rho_{\text{min}} = -0.21 \) 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. All non-hydrogen atoms were refined anisotropically. H atoms bound to C atoms were constrained to ride on the atoms onto which they are bonded, where C—H = 0.95 (aromatic) or 0.98 Å (methyl) with \( U_{eq}(H) = 1.2U_{eq}(C) \).
Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|    | x       | y       | z       | U(eq)         |
|----|---------|---------|---------|---------------|
| Cl1| 0.81953 (5) | 0.48342 (4) | 0.83259 (3) | 0.02349 (9)    |
| Cl2| 0.74478 (5) | 0.08068 (4) | 0.71750 (3) | 0.02487 (9)    |
| O1 | 0.76916 (17) | 0.76700 (12) | 0.40055 (10) | 0.0310 (2)     |
| O2 | 0.69277 (14) | 0.55617 (11) | 0.22210 (9)  | 0.02121 (18)   |
| O3 | 0.50933 (14) | 0.17388 (12) | 0.16137 (9)  | 0.02470 (19)   |
| O4 | 0.84744 (13) | 0.20884 (11) | 0.21752 (8)  | 0.02113 (18)   |
| O1 | 0.73795 (16) | 0.47447 (14) | 0.43804 (11) | 0.0158 (2)     |
| O2 | 0.77075 (17) | 0.53010 (15) | 0.57530 (12) | 0.0170 (2)     |
| O3 | 0.7904       | 0.6508    | 0.6094    | 0.020*         |
| O4 | 0.77483 (17) | 0.41014 (15) | 0.66231 (11) | 0.0172 (2)     |
| C5 | 0.71216 (18) | 0.17662 (15) | 0.47593 (12) | 0.0185 (2)     |
| H5 | 0.6921       | 0.0558    | 0.4423    | 0.022*         |
| C6 | 0.70903 (17) | 0.29623 (14) | 0.38820 (11) | 0.0159 (2)     |
| C7 | 0.73570 (17) | 0.61539 (15) | 0.35369 (12) | 0.0179 (2)     |
| C8 | 0.6829 (2)   | 0.68909 (17)| 0.13612 (13) | 0.0247 (3)     |
| H8A| 0.6390       | 0.6352    | 0.0408    | 0.037*         |
| H8B| 0.8168       | 0.7473    | 0.1603    | 0.037*         |
| H8C| 0.5863       | 0.7746    | 0.1491    | 0.037*         |
| C9 | 0.67274 (18) | 0.22206 (14) | 0.24202 (12) | 0.0175 (2)     |
| C10| 0.8297 (2)   | 0.14662 (17)| 0.07783 (12) | 0.0249 (3)     |
| H10A| 0.7640      | 0.2330    | 0.0200    | 0.037*         |
| H10B| 0.7485       | 0.0365    | 0.0474    | 0.037*         |
| H10C| 0.9646       | 0.1283    | 0.0717    | 0.037*         |

Atomic displacement parameters (Å²)

|     | Uᵢ₁     | Uᵢ₂     | Uᵢ₃     | Uᵢ₂₃    | Uᵢ₁₂    | Uᵢ₁₃    |
|-----|---------|---------|---------|---------|---------|---------|
| Cl1 | 0.02835 (16) | 0.02741 (16) | 0.01490 (15) | −0.00009 (11) | 0.00920 (12) | −0.00131 (11) |
| Cl2 | 0.03392 (18) | 0.02289 (16) | 0.01804 (15) | −0.00098 (12) | 0.00730 (12) | 0.00740 (11) |
| O1  | 0.0505 (6) | 0.0152 (4) | 0.0266 (5) | 0.0004 (4) | 0.0124 (4) | 0.0022 (3) |
| O2  | 0.0281 (4) | 0.0181 (4) | 0.0175 (4) | −0.0003 (3) | 0.0066 (3) | 0.0052 (3) |
| O3  | 0.0253 (5) | 0.0269 (4) | 0.0174 (4) | −0.0058 (3) | 0.0021 (3) | 0.0010 (3) |
| O4  | 0.0235 (4) | 0.0248 (4) | 0.0136 (4) | 0.0029 (3) | 0.0056 (3) | −0.0005 (3) |
| C1  | 0.0142 (5) | 0.0158 (5) | 0.0169 (5) | 0.0010 (4) | 0.0045 (4) | 0.0026 (4) |
| C2  | 0.0152 (5) | 0.0161 (5) | 0.0188 (5) | 0.0008 (4) | 0.0056 (4) | −0.0004 (4) |
| C3  | 0.0156 (5) | 0.0217 (5) | 0.0139 (5) | 0.0011 (4) | 0.0052 (4) | 0.0000 (4) |
| C4  | 0.0183 (5) | 0.0196 (5) | 0.0164 (5) | 0.0003 (4) | 0.0049 (4) | 0.0050 (4) |
| C5  | 0.0216 (5) | 0.0155 (5) | 0.0171 (5) | −0.0003 (4) | 0.0048 (4) | 0.0019 (4) |
| C6  | 0.0155 (5) | 0.0165 (5) | 0.0143 (5) | 0.0002 (4) | 0.0034 (4) | 0.0011 (4) |
| C7  | 0.0168 (5) | 0.0167 (5) | 0.0204 (5) | 0.0019 (4) | 0.0059 (4) | 0.0036 (4) |
| C8  | 0.0292 (6) | 0.0237 (6) | 0.0243 (6) | 0.0038 (5) | 0.0098 (5) | 0.0115 (5) |
| C9  | 0.0242 (6) | 0.0125 (5) | 0.0150 (5) | 0.0009 (4) | 0.0049 (4) | 0.0030 (4) |
| C10 | 0.0342 (7) | 0.0261 (6) | 0.0147 (5) | 0.0029 (5) | 0.0097 (5) | −0.0001 (4) |
Geometric parameters (Å, °)

| Bond/Angle | Distance       | Bond/Angle | Distance       |
|------------|----------------|------------|----------------|
| Cl1—C3     | 1.7305 (12)    | C2—C3      | 1.3865 (16)    |
| Cl2—C4     | 1.7272 (12)    | C3—C4      | 1.3931 (16)    |
| O1—C7      | 1.2042 (15)    | C4—C5      | 1.3871 (16)    |
| O2—C7      | 1.3330 (15)    | C5—H5      | 0.9500         |
| O2—C8      | 1.4500 (14)    | C6—C9      | 1.3915 (15)    |
| O3—C9      | 1.2202 (15)    | C8—H8A     | 0.9800         |
| O4—C9      | 1.3359 (15)    | C8—H8B     | 0.9800         |
| O4—C10     | 1.4503 (14)    | C8—H8C     | 0.9800         |
| C1—C2      | 1.3940 (16)    | C8—H8A     | 109.5          |
| C1—C6      | 1.4018 (15)    | C8—H8B     | 109.5          |
| C1—C7      | 1.4969 (15)    | C8—H8C     | 109.5          |
| C2—H2      | 0.9500         | C10—H10A   | 109.5          |
| C7—O2—C8   | 115.05 (9)     | C10—H10B   | 109.5          |
| C9—O4—C10  | 115.31 (10)    | C10—H10C   | 109.5          |
| C2—C1—C6   | 119.63 (10)    | C5—C6—C9  | 109.5          |
| C2—C1—C7   | 115.67 (10)    | O1—C7—O2  | 109.5          |
| C6—C1—C7   | 124.70 (10)    | O1—C7—C1  | 109.5          |
| C1—C2—H2   | 119.8          | O2—C8—H8A | 109.5          |
| C3—C2—C1   | 120.33 (10)    | O2—C8—H8B | 109.5          |
| C3—C2—H2   | 119.8          | O2—C8—H8C | 109.5          |
| C2—C3—Cl1  | 119.14 (9)     | H8A—C8—H8B| 109.5          |
| C2—C3—C4   | 119.92 (10)    | H8A—C8—H8C| 109.5          |
| C4—C3—Cl1  | 120.94 (9)     | O3—C9—O4  | 109.5          |
| C4—C3—Cl2  | 121.06 (9)     | O3—C9—C6  | 109.5          |
| C5—C4—Cl2  | 118.80 (9)     | O4—C9—C6  | 109.5          |
| C5—C4—C3   | 120.14 (10)    | O4—C10—H10A| 109.5         |
| C4—C5—H5   | 119.9          | O4—C10—H10B| 109.5         |
| C4—C5—C6   | 120.23 (10)    | O4—C10—H10C| 109.5         |
| C6—C5—H5   | 119.9          | H10A—C10—H10B| 109.5       |
| C1—C6—C9   | 124.00 (10)    | H10A—C10—H10C| 109.5     |
| C5—C6—C1   | 119.74 (10)    | H10B—C10—H10C| 109.5    |

C11—C3—C4—Cl2  | 1.42 (14) | C4—C5—C6—C1  | −0.23 (17)  |
C11—C3—C4—C5   | −178.93 (9)| C4—C5—C6—C9  | −179.96 (10)|
C12—C4—C5—C6   | 179.38 (9)| C5—C6—C9—O3  | 78.67 (15)  |
C1—C2—C3—Cl1   | 179.08 (9)| C5—C6—C9—O4  | −97.92 (12) |
C1—C2—C3—C4   | −0.50 (17) | C6—C1—C2—C3  | 0.00 (17)   |
C1—C6—C9—O3   | −101.05 (14)| C6—C1—C7—O1 | −176.90 (12)|
C1—C6—C9—O4   | 82.36 (13) | C6—C1—C7—O2  | 3.20 (16)   |
C2—C1—C6—C5   | 0.37 (17)  | C7—C1—C2—C3  | 179.72 (10) |
C2—C1—C6—C9   | −179.92 (10)| C7—C1—C6—C5  | −179.33 (10)|
C2—C1—C7—O1   | 3.39 (17)  | C7—C1—C6—C9  | 0.38 (18)   |
C2—C1—C7—O2   | −176.51 (10)| C8—O2—C7—O1 | −1.71 (17)  |
C2—C3—C4—Cl2  | −179.00 (8) | C8—O2—C7—C1 | 178.18 (9)  |
C2—C3—C4—C5   | 0.65 (17)  | C10—O4—C9—O3 | 6.33 (17)   |
$\text{C3—C4—C5—C6}$ $-0.28$ (18) $\text{C10—O4—C9—C6}$ $-177.12$ (9)

**Hydrogen-bond geometry (Å, °)**

|                | $D$—H | $H$···$A$ | $D$···$A$ | $D$—H···$A$ |
|----------------|-------|-----------|-----------|-------------|
| $\text{C5—H5} \cdots \text{O1}^i$ | 0.95  | 2.33      | 3.2327 (15)| 159         |
| $\text{C10—H10B} \cdots \text{O3}^ii$ | 0.98  | 2.68      | 3.5380 (16)| 147         |

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, -y, -z$. 