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1,3,5-Trichloro-2-methoxybenzene

Sanjay Telu,^a Sean Parkin,^b Larry W. Robertson^a and Hans-Joachim Lehmler^{a*}

^aDepartment of Occupational and Environmental Health, University of Iowa, 100 Oakdale Campus, 124 IREH, Iowa City, IA 52242-5000, USA, and ^bDepartment of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA
Correspondence e-mail: hans-joachim-lehmler@uiowa.edu

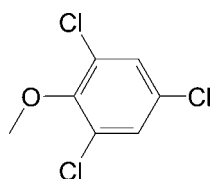
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Key indicators: single-crystal X-ray study; $T = 90$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.030; wR factor = 0.071; data-to-parameter ratio = 18.7.

The methoxy group of the title compound, $\text{C}_7\text{H}_5\text{Cl}_3\text{O}$, is rotated out of the plane of the aromatic ring system, with a dihedral angle of $84.11(13)^\circ$, due to the two bulky *ortho*-chloro substituents.

Related literature

For similar structures of anisoles with two *ortho*-chloro substituents, see: Rissanen *et al.* (1987); Weller & Gerstner (1995); Wiczorek (1980). For other related literature, see: Brownlee *et al.* (1993); Curtis *et al.* (1972); Iimura *et al.* (1984); Kolehmainen & Knuutinen (1983); Oswald *et al.* (2005); Pereira *et al.* (2000); Rissanen *et al.* (1988); Vlachos *et al.* (2007); Zhang *et al.* (2006).



Experimental

Crystal data

$\text{C}_7\text{H}_5\text{Cl}_3\text{O}$
 $M_r = 211.46$
Monoclinic, $P2_1/n$
 $a = 14.7538(5)$ Å
 $b = 3.9846(2)$ Å
 $c = 15.4810(7)$ Å
 $\beta = 115.5031(19)^\circ$

$V = 821.42(6)$ Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 1.05$ mm⁻¹
 $T = 90.0(2)$ K
 $0.25 \times 0.25 \times 0.12$ mm

Data collection

| | |
|---|--|
| Nonius KappaCCD area-detector diffractometer | 13489 measured reflections |
| Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997) | 1888 independent reflections |
| $T_{\min} = 0.780$, $T_{\max} = 0.885$ | 1558 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.020$ |

Refinement

| | |
|---------------------------------|---|
| $R[F^2 > 2\sigma(F^2)] = 0.030$ | 101 parameters |
| $wR(F^2) = 0.070$ | H-atom parameters constrained |
| $S = 1.13$ | $\Delta\rho_{\max} = 0.35$ e Å ⁻³ |
| 1888 reflections | $\Delta\rho_{\min} = -0.31$ e Å ⁻³ |

Data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO-SMN (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP in SHELXTL (Sheldrick, 1994); software used to prepare material for publication: SHELX97 and local procedures.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2200).

References

- Brownlee, B. G., MacInnis, G. A. & Noton, L. R. (1993). *Environ. Sci. Technol.* **27**, 2450–2455.
- Curtis, R. F., Land, D. G., Griffiths, N. M., Gee, M., Robinson, D., Peel, J. L., Dennis, C. & Gee, J. M. (1972). *Nature (London)*, **235**, 223–224.
- Iimura, Y., Sakurai, T., Asahi, K.-I., Takahashi, N. & Oka, H. (1984). *Acta Cryst.* **C40**, 2058–2061.
- Kolehmainen, E. & Knuutinen, J. (1983). *Org. Magn. Reson.* **21**, 388–390.
- Nonius (1998). COLLECT. Nonius BV, Delft, The Netherlands.
- Oswald, I. D. H., Allan, D. R., Day, G. M., Motherwell, W. D. S. & Parsons, S. (2005). *Cryst. Growth Des.* **5**, 1055–1071.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Pereira, C. S., Marques, J. J. F. & San Romao, M. V. (2000). *Crit. Rev. Microbiol.* **26**, 147–162.
- Rissanen, K., Valkonen, J. & Knuutinen, J. (1987). *Acta Cryst.* **C43**, 1966–1968.
- Rissanen, K., Valkonen, J. & Mannila, B. (1988). *Acta Cryst.* **C44**, 684–686.
- Sheldrick, G. M. (1994). SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Vlachos, P., Kampioti, A., Kornaros, M. & Lyberatos, G. (2007). *Eur. Food Res. Technol.* **225**, 653–663.
- Weller, F. & Gerstner, E. (1995). *Z. Kristallogr.* **210**, 629–629.
- Wiczorek, M. W. (1980). *Acta Cryst.* **B36**, 1515–1517.
- Zhang, L., Hu, R. & Yang, Z. (2006). *Water Sci. Technol.* **54**, 335–344.

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1,3,5-Trichloro-2-methoxybenzene

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S1. Comment

Chlorinated anisoles are persistent environmental pollutants known for their toxicity and tendency to bioaccumulate (Brownlee *et al.*, 1993). Especially anisoles with chlorine substitution in the 2- and 6- position are a well known cause for off-flavors in water, fish and chicken eggs (Brownlee *et al.*, 1993; Curtis *et al.*, 1972; Zhang *et al.*, 2006). The title compound is a major contributor to "cork taint", a well known off-flavor in the wine industry (Pereira *et al.*, 2000; Vlachos *et al.*, 2007). We herin report the molecular structure of the title compound to aid in structure activity relationship (SAR) studies of the toxicity of chlorinated anisoles.

It has been reported that *ortho*-disubstitution causes drastic changes in the spatial arrangement of the methoxy group of chlorinated anisols, both in solution and in the solid state (Kolehmainen & Knuutinen, 1983; Rissanen *et al.*, 1987). In the title compound, the methoxy group was rotated out of the plane of the phenyl ring with a dihedral angle of 84.11 (13)°. The angle was calculated between the plane of the benzene ring (C1 through C6) and the methoxy group (atoms C1,O1,C7). Comparable anisoles have similar dihedral angles ranging from 76.8 to 92.1° (Iimura *et al.*, 1984; Rissanen *et al.*, 1987; Rissanen *et al.*, 1988; Weller & Gerstner, 1995; Wieczorek, 1980). In contrast, the methoxy group of non-*ortho* substituted anisoles lies within the plane of the phenyl ring.

The O—CH₃ bond length of the title compound (O1—C7: 1.446 (2) Å) was larger compared to non-*ortho* substituted anisoles, which have a mean bond length of 1.422 Å. Furthermore, the C_{Ar}—O—CH₃ bond angle of the title compound (C1—O1—C7: 114.60 (15)°) was smaller compared to non-*ortho* substituted anisoles, which is on average 117.73°. Chlorine disubstitution *ortho* to an aromatic methoxy group had a similar effect on the O—CH₃ bond length and the C_{Ar}—O—CH₃ bond angles in several structurally related compounds (Iimura *et al.*, 1984; Rissanen *et al.*, 1987; Rissanen *et al.*, 1988; Weller & Gerstner, 1995; Wieczorek, 1980).

Ortho disubstitution forced the methoxy group out of the plane of the aromatic ring, so that the CH₃ group (C7) of the title compound was located 1.192 (4) Å above and the O1 atom -0.079 (3)Å below the calculated least-squares plane of the benzene ring. In other, structurally related compounds with *ortho* dichloro substitution, the O atoms are positioned 0.030 to 0.133 Å below and the methoxy C atoms 1.119 to 1.252 Å above the calculated last-squares plane (Iimura *et al.*, 1984; Rissanen *et al.*, 1987; Rissanen *et al.*, 1988; Weller & Gerstner, 1995; Wieczorek, 1980). Overall, this difference in the spatial arrangement of the methoxy group is thought to explain the off-flavor of anisoles with *ortho* disubstitution.

S2. Experimental

Crystals of the title compound suitable for crystal structure analysis were obtained from TCI America (Portland, Oregon, USA.).

S3. Refinement

H atoms were found in difference Fourier maps and subsequently placed in idealized positions with constrained C—H distances of 0.98 Å ($C_{Me}H$) and 0.95 Å ($C_{Ar}H$) with $U_{iso}(H)$ values set to either $1.5U_{eq}(C_{Me}H)$ or $1.2U_{eq}(C_{Ar}H)$ of the attached C atom respectively.

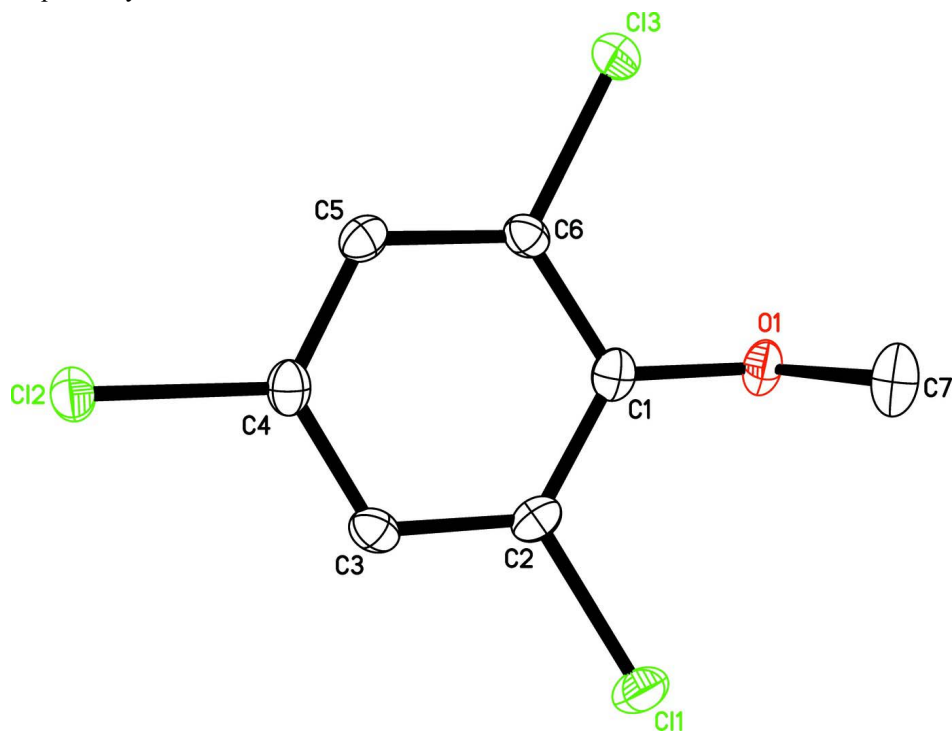


Figure 1

View of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

1,3,5-Trichloro-2-methoxybenzene

Crystal data

$C_7H_5Cl_3O$
 $M_r = 211.46$
 Monoclinic, $P2_1/n$
 Hall symbol: -P 2yn
 $a = 14.7538$ (5) Å
 $b = 3.9846$ (2) Å
 $c = 15.4810$ (7) Å
 $\beta = 115.5031$ (19)°
 $V = 821.42$ (6) Å³
 $Z = 4$

$F(000) = 424$
 $D_x = 1.710$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2156 reflections
 $\theta = 1.0$ – 27.5°
 $\mu = 1.05$ mm⁻¹
 $T = 90$ K
 Block, colourless
 $0.25 \times 0.25 \times 0.12$ mm

Data collection

Nonius KappaCCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Detector resolution: 18 pixels mm⁻¹
 ω scans at fixed $\chi = 55^\circ$

Absorption correction: multi-scan
 (SCALEPACK; Otwinowski & Minor, 1997)
 $T_{min} = 0.780$, $T_{max} = 0.885$
 13489 measured reflections
 1888 independent reflections
 1558 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$
 $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 1.6^\circ$
 $h = -18 \rightarrow 19$

$k = -5 \rightarrow 5$
 $l = -20 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.070$
 $S = 1.13$
 1888 reflections
 101 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
 $w = 1/[\sigma^2(F_o^2) + (0.0244P)^2 + 0.6499P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.35 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{\AA}^{-3}$

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| C11 | 0.65436 (3) | 0.31728 (13) | 0.83292 (3) | 0.02202 (13) |
| C12 | 0.36963 (3) | 0.90882 (13) | 0.91077 (3) | 0.01965 (12) |
| C13 | 0.32350 (3) | 0.84337 (13) | 0.54775 (3) | 0.02053 (13) |
| O1 | 0.51708 (9) | 0.4751 (4) | 0.63059 (9) | 0.0189 (3) |
| C1 | 0.48575 (13) | 0.5887 (5) | 0.69659 (13) | 0.0161 (4) |
| C2 | 0.54027 (13) | 0.5242 (5) | 0.79404 (13) | 0.0161 (4) |
| C3 | 0.50643 (13) | 0.6209 (5) | 0.86111 (13) | 0.0162 (4) |
| H3 | 0.5447 | 0.5753 | 0.9273 | 0.019* |
| C4 | 0.41531 (14) | 0.7858 (5) | 0.82874 (13) | 0.0164 (4) |
| C5 | 0.35818 (13) | 0.8564 (5) | 0.73309 (13) | 0.0158 (4) |
| H5 | 0.2958 | 0.9705 | 0.7126 | 0.019* |
| C6 | 0.39426 (13) | 0.7561 (5) | 0.66748 (12) | 0.0147 (4) |
| C7 | 0.58710 (16) | 0.6940 (6) | 0.61549 (15) | 0.0253 (5) |
| H7A | 0.5565 | 0.9156 | 0.5951 | 0.038* |
| H7B | 0.6039 | 0.5988 | 0.5659 | 0.038* |
| H7C | 0.6483 | 0.7159 | 0.6753 | 0.038* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|--------------|--------------|---------------|
| C11 | 0.0146 (2) | 0.0252 (3) | 0.0231 (2) | 0.00407 (19) | 0.00509 (19) | -0.0021 (2) |
| C12 | 0.0178 (2) | 0.0266 (3) | 0.0163 (2) | 0.00018 (18) | 0.00906 (18) | -0.00204 (18) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C13 | 0.0190 (2) | 0.0279 (3) | 0.0139 (2) | 0.00294 (19) | 0.00632 (18) | 0.00251 (18) |
| O1 | 0.0171 (7) | 0.0230 (8) | 0.0205 (7) | -0.0022 (6) | 0.0119 (6) | -0.0046 (6) |
| C1 | 0.0160 (9) | 0.0152 (10) | 0.0188 (9) | -0.0037 (7) | 0.0092 (7) | -0.0036 (7) |
| C2 | 0.0123 (8) | 0.0142 (10) | 0.0208 (9) | -0.0003 (7) | 0.0061 (7) | -0.0008 (7) |
| C3 | 0.0152 (9) | 0.0177 (10) | 0.0129 (8) | -0.0030 (7) | 0.0035 (7) | -0.0009 (7) |
| C4 | 0.0177 (9) | 0.0160 (10) | 0.0184 (9) | -0.0037 (7) | 0.0106 (8) | -0.0031 (7) |
| C5 | 0.0128 (8) | 0.0155 (10) | 0.0192 (9) | -0.0002 (7) | 0.0069 (7) | 0.0005 (7) |
| C6 | 0.0138 (9) | 0.0168 (10) | 0.0120 (8) | -0.0023 (7) | 0.0040 (7) | 0.0002 (7) |
| C7 | 0.0273 (11) | 0.0255 (11) | 0.0310 (11) | -0.0054 (9) | 0.0201 (9) | -0.0052 (9) |

Geometric parameters (Å, °)

| | | | |
|--------------|--------------|--------------|--------------|
| C1—O1 | 1.367 (2) | C13—C6 | 1.7264 (18) |
| C1—C2 | 1.394 (3) | C4—C5 | 1.381 (3) |
| C1—C6 | 1.395 (3) | C5—C6 | 1.393 (3) |
| C2—C3 | 1.386 (3) | C5—H5 | 0.9500 |
| C2—C11 | 1.7329 (19) | O1—C7 | 1.446 (2) |
| C3—C4 | 1.382 (3) | C7—H7A | 0.9800 |
| C3—H3 | 0.9500 | C7—H7B | 0.9800 |
| C12—C4 | 1.7447 (18) | C7—H7C | 0.9800 |
| O1—C1—C2 | 121.63 (16) | C4—C5—H5 | 120.8 |
| O1—C1—C6 | 120.55 (16) | C6—C5—H5 | 120.8 |
| C2—C1—C6 | 117.70 (16) | C5—C6—C1 | 121.46 (16) |
| C3—C2—C1 | 122.21 (17) | C5—C6—C13 | 118.74 (14) |
| C3—C2—C11 | 118.77 (14) | C1—C6—C13 | 119.79 (14) |
| C1—C2—C11 | 119.02 (14) | C1—O1—C7 | 114.60 (15) |
| C4—C3—C2 | 117.92 (17) | O1—C7—H7A | 109.5 |
| C4—C3—H3 | 121.0 | O1—C7—H7B | 109.5 |
| C2—C3—H3 | 121.0 | H7A—C7—H7B | 109.5 |
| C5—C4—C3 | 122.34 (17) | O1—C7—H7C | 109.5 |
| C5—C4—C12 | 118.33 (14) | H7A—C7—H7C | 109.5 |
| C3—C4—C12 | 119.33 (14) | H7B—C7—H7C | 109.5 |
| C4—C5—C6 | 118.36 (17) | | |
| O1—C1—C2—C3 | -176.17 (17) | C12—C4—C5—C6 | -179.55 (14) |
| C6—C1—C2—C3 | -0.1 (3) | C4—C5—C6—C1 | -0.1 (3) |
| O1—C1—C2—C11 | 4.0 (3) | C4—C5—C6—C13 | -179.94 (14) |
| C6—C1—C2—C11 | -179.91 (14) | O1—C1—C6—C5 | 176.18 (17) |
| C1—C2—C3—C4 | 0.1 (3) | C2—C1—C6—C5 | 0.1 (3) |
| C11—C2—C3—C4 | 179.96 (15) | O1—C1—C6—C13 | -4.0 (3) |
| C2—C3—C4—C5 | -0.2 (3) | C2—C1—C6—C13 | 179.92 (14) |
| C2—C3—C4—C12 | 179.51 (15) | C2—C1—O1—C7 | -86.2 (2) |
| C3—C4—C5—C6 | 0.1 (3) | C6—C1—O1—C7 | 97.9 (2) |