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Methanaminium 3,4,5,6-tetrachloro-2-(methoxycarbonyl)benzoate

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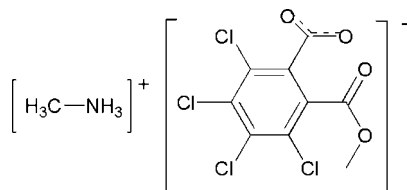
Received 22 January 2011; accepted 5 February 2011

 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.034; wR factor = 0.092; data-to-parameter ratio = 13.7.

In the crystal structure of the title compound, $\text{CH}_6\text{N}^+\text{-C}_9\text{H}_3\text{Cl}_4\text{O}_4^-$, the N atom of the methylamine molecule is protonated and hydrogen bonded to the carboxyl group of the 3,4,5,6-tetrachloro-2-(methoxycarbonyl)benzoate anion. The anions are linked by the cations *via* intermolecular $\text{N}-\text{H}\cdots\text{O}$ interactions into chains extending along the c axis.

Related literature

For related structures, see: Li (2011); Liang (2008).



Experimental

Crystal data

 $\text{CH}_6\text{N}^+\text{-C}_9\text{H}_3\text{Cl}_4\text{O}_4^-$
 $M_r = 348.98$
 Monoclinic, $P2_1/c$
 $a = 14.3138$ (13) Å
 $b = 14.2231$ (14) Å
 $c = 6.7648$ (7) Å

 $\beta = 91.021$ (1)°
 $V = 1377.0$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

 $\mu = 0.87$ mm⁻¹
 $T = 298$ K
 $0.45 \times 0.40 \times 0.38$ mm

Data collection

 Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
 $T_{\min} = 0.697$, $T_{\max} = 0.734$

 6756 measured reflections
 2413 independent reflections
 1752 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.092$
 $S = 1.06$
 2413 reflections

 176 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1A}\cdots\text{O3}^{\text{i}}$	0.89	1.86	2.742 (3)	173
$\text{N1}-\text{H1B}\cdots\text{O4}^{\text{ii}}$	0.89	1.93	2.794 (3)	163
$\text{N1}-\text{H1C}\cdots\text{O4}$	0.89	1.92	2.797 (3)	170

 Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2219).

References

- Bruker (1997). *SADABS*, *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
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 Liang, Z.-P. (2008). *Acta Cryst.* **E64**, o2416.
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supporting information

Acta Cryst. (2011). E67, o605 [doi:10.1107/S1600536811004351]

Methanaminium 3,4,5,6-tetrachloro-2-(methoxycarbonyl)benzoate

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S1. Comment

Crystals of the title compound were obtained by accident by the reaction of 2-(methoxycarbonyl)-3,4,5,6-tetrachlorobenzoic acid and methanamine in methanol. To identify the product of this reaction a single crystal structure analysis was performed.

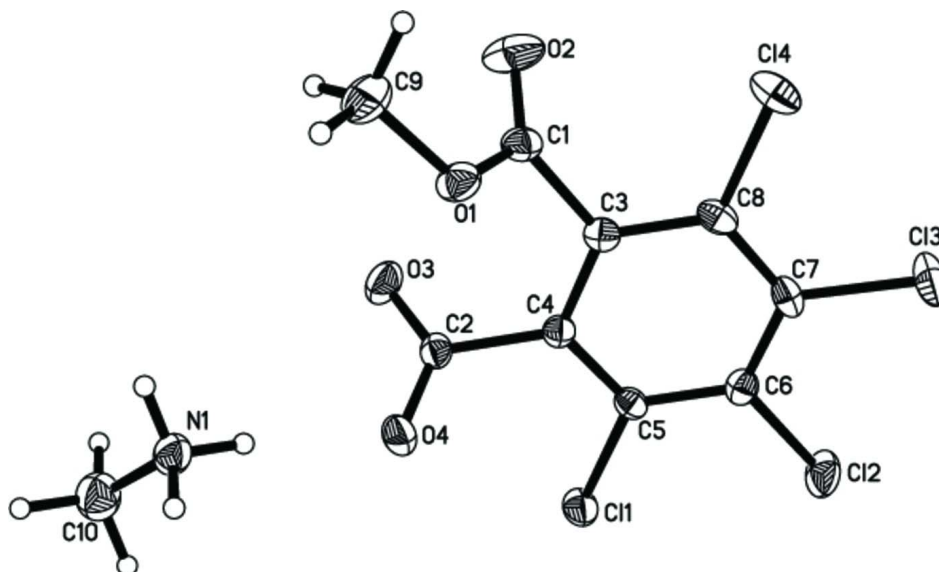
The asymmetric unit of the title compound (I) contains one methylammonium cation and one 2-(methoxycarbonyl)-3,4,5,6-tetrachlorobenzoate anion (Fig. 1). The bond lengths and angles are in agreement with those in ethylammonium 2-(methoxycarbonyl)-3,4,5,6-tetrabromobenzoate methanol solvate (Li, 2011) and in ethane-1,2-diammonium bis(2-(methoxycarbonyl)-3,4,5,6-tetrabromobenzoate) methanol solvate (Liang, 2008). In the crystal structure the cations and anions are connected by intermolecular N—H \cdots O hydrogen bonding into chains that elongate in the direction of the crystallographic c-axis (Fig. 2). Moreover, short distances between chlorine and oxygen atoms are found indicating for intermolecular Cl—O interactions (Fig. 2).

S2. Experimental

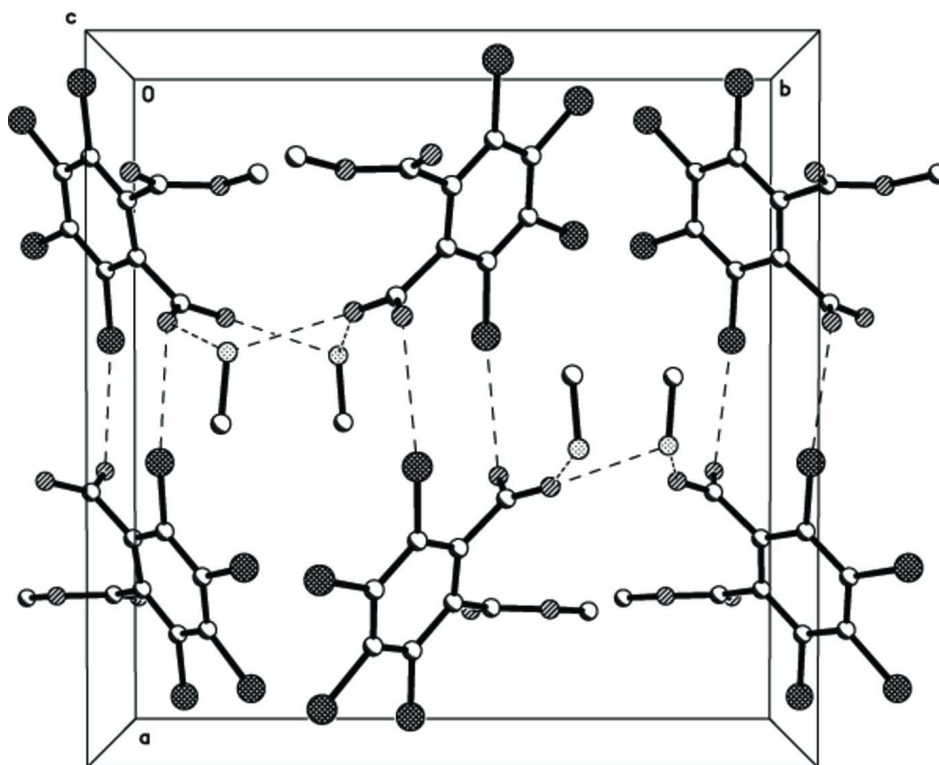
A mixture of 2-(methoxycarbonyl)-3,4,5,6-tetrachlorobenzoic acid (2.86 g, 0.01 mol) and methanol (15 ml) was refluxed for 0.5 h. Afterwards methanamine (0.45 g, 0.01 mol) was added and the mixture was stirred for 10 min at room temperature. The solution was kept at room temperature for 5 d. On solvent evaporation colourless single crystals of the title compound were obtained that are suitable for X-ray analysis.

S3. Refinement

H atoms were initially located from difference maps and then refined in a riding model with C—H = 0.96–0.97 Å, N—H = 0.89 Å, O—H = 0.82 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O, N, methyl C})$.

**Figure 1**

The molecular structure of the title compound with labelling and 30% probability ellipsoids.

**Figure 2**

Crystal structure of the title compound viewed along the *c* axis. Hydrogen bonding and Cl...O interactions are shown as dashed lines.

Methanaminium 3,4,5,6-tetrachloro-2-(methoxycarbonyl)benzoate*Crystal data*CH₆N⁺·C₉H₃Cl₄O₄⁻ $M_r = 348.98$ Monoclinic, $P2_1/c$ $a = 14.3138$ (13) Å $b = 14.2231$ (14) Å $c = 6.7648$ (7) Å $\beta = 91.021$ (1)° $V = 1377.0$ (2) Å³ $Z = 4$ $F(000) = 704$ $D_x = 1.683$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2427 reflections

 $\theta = 2.9$ – 27.9 ° $\mu = 0.87$ mm⁻¹ $T = 298$ K

Block, colorless

 $0.45 \times 0.40 \times 0.38$ mm*Data collection*Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

phi and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 1997)

 $T_{\min} = 0.697$, $T_{\max} = 0.734$

6756 measured reflections

2413 independent reflections

1752 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.034$ $\theta_{\max} = 25.0$ °, $\theta_{\min} = 2.9$ ° $h = -10$ → 17 $k = -16$ → 15 $l = -8$ → 7 *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.092$ $S = 1.06$

2413 reflections

176 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 0.764P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.27$ e Å⁻³ $\Delta\rho_{\min} = -0.26$ e Å⁻³Extinction correction: SHELXL97 (Sheldrick,
2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0169 (12)

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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.59548 (5)	0.44954 (5)	0.68418 (11)	0.0403 (2)
Cl2	0.75122 (6)	0.31368 (5)	0.83762 (13)	0.0504 (3)
Cl3	0.94431 (6)	0.31160 (6)	0.64018 (14)	0.0560 (3)

C14	0.97935 (5)	0.43587 (5)	0.26682 (13)	0.0498 (3)
N1	0.56810 (18)	0.82381 (16)	0.3492 (4)	0.0405 (6)
H1A	0.5878	0.8600	0.4489	0.061*
H1B	0.5950	0.8422	0.2382	0.061*
H1C	0.5832	0.7642	0.3743	0.061*
O1	0.82037 (15)	0.65000 (13)	0.1792 (3)	0.0405 (5)
O2	0.8307 (2)	0.52896 (16)	-0.0279 (3)	0.0647 (7)
O3	0.61656 (15)	0.57063 (15)	0.1743 (3)	0.0481 (6)
O4	0.62782 (14)	0.64439 (13)	0.4641 (3)	0.0408 (5)
C1	0.82003 (19)	0.5598 (2)	0.1337 (4)	0.0345 (7)
C2	0.64751 (19)	0.58072 (18)	0.3451 (4)	0.0303 (6)
C3	0.80417 (19)	0.50129 (17)	0.3163 (4)	0.0282 (6)
C4	0.71960 (19)	0.50884 (17)	0.4148 (4)	0.0269 (6)
C5	0.70398 (18)	0.44908 (17)	0.5740 (4)	0.0274 (6)
C6	0.77229 (19)	0.38691 (18)	0.6410 (4)	0.0303 (6)
C7	0.85805 (19)	0.38385 (18)	0.5494 (4)	0.0325 (7)
C8	0.87294 (19)	0.43961 (18)	0.3837 (4)	0.0327 (7)
C9	0.8303 (3)	0.7137 (2)	0.0141 (5)	0.0592 (10)
H9A	0.8873	0.7001	-0.0528	0.089*
H9B	0.8319	0.7773	0.0617	0.089*
H9C	0.7783	0.7061	-0.0760	0.089*
C10	0.4658 (2)	0.8321 (2)	0.3267 (5)	0.0543 (9)
H10A	0.4367	0.8127	0.4468	0.082*
H10B	0.4444	0.7928	0.2197	0.082*
H10C	0.4495	0.8963	0.2988	0.082*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0319 (4)	0.0426 (4)	0.0470 (5)	0.0041 (3)	0.0120 (3)	0.0124 (3)
C12	0.0489 (5)	0.0470 (5)	0.0554 (5)	0.0046 (4)	0.0012 (4)	0.0251 (4)
C13	0.0397 (5)	0.0524 (5)	0.0758 (6)	0.0189 (4)	-0.0053 (4)	0.0093 (4)
C14	0.0323 (4)	0.0515 (5)	0.0660 (6)	0.0021 (4)	0.0166 (4)	-0.0093 (4)
N1	0.0551 (17)	0.0323 (13)	0.0341 (14)	0.0043 (12)	-0.0040 (12)	-0.0006 (11)
O1	0.0548 (14)	0.0320 (11)	0.0350 (11)	-0.0030 (10)	0.0087 (10)	0.0036 (9)
O2	0.097 (2)	0.0604 (15)	0.0369 (14)	-0.0146 (14)	0.0208 (13)	-0.0099 (11)
O3	0.0471 (13)	0.0616 (14)	0.0352 (12)	0.0050 (11)	-0.0105 (10)	0.0095 (10)
O4	0.0451 (13)	0.0313 (11)	0.0462 (13)	0.0112 (9)	0.0059 (10)	0.0040 (9)
C1	0.0297 (16)	0.0423 (17)	0.0317 (17)	-0.0031 (13)	0.0049 (13)	-0.0011 (13)
C2	0.0264 (15)	0.0295 (15)	0.0352 (17)	0.0005 (12)	0.0043 (13)	0.0089 (13)
C3	0.0310 (15)	0.0240 (13)	0.0295 (15)	-0.0035 (12)	0.0012 (12)	-0.0042 (11)
C4	0.0284 (15)	0.0263 (14)	0.0261 (14)	-0.0004 (12)	-0.0011 (12)	-0.0018 (11)
C5	0.0226 (14)	0.0283 (14)	0.0314 (15)	-0.0005 (12)	0.0022 (12)	-0.0028 (12)
C6	0.0341 (16)	0.0252 (14)	0.0315 (15)	-0.0017 (12)	-0.0027 (13)	0.0011 (11)
C7	0.0260 (15)	0.0258 (14)	0.0454 (17)	0.0046 (12)	-0.0043 (13)	-0.0050 (12)
C8	0.0296 (15)	0.0294 (14)	0.0391 (17)	-0.0011 (12)	0.0060 (13)	-0.0095 (13)
C9	0.074 (3)	0.051 (2)	0.054 (2)	-0.0026 (19)	0.0147 (19)	0.0210 (17)
C10	0.055 (2)	0.054 (2)	0.053 (2)	0.0031 (17)	-0.0051 (18)	0.0001 (16)

Geometric parameters (Å, °)

C11—C5	1.734 (3)	C2—C4	1.521 (4)
C12—C6	1.720 (3)	C3—C8	1.389 (4)
C13—C7	1.712 (3)	C3—C4	1.396 (4)
C14—C8	1.729 (3)	C4—C5	1.393 (4)
N1—C10	1.475 (4)	C5—C6	1.388 (4)
N1—H1A	0.8900	C6—C7	1.386 (4)
N1—H1B	0.8900	C7—C8	1.393 (4)
N1—H1C	0.8900	C9—H9A	0.9600
O1—C1	1.319 (3)	C9—H9B	0.9600
O1—C9	1.447 (3)	C9—H9C	0.9600
O2—C1	1.191 (3)	C10—H10A	0.9600
O3—C2	1.238 (3)	C10—H10B	0.9600
O4—C2	1.247 (3)	C10—H10C	0.9600
C1—C3	1.510 (4)		
C10—N1—H1A	109.5	C7—C6—C5	119.9 (2)
C10—N1—H1B	109.5	C7—C6—C12	119.7 (2)
H1A—N1—H1B	109.5	C5—C6—C12	120.4 (2)
C10—N1—H1C	109.5	C6—C7—C8	119.5 (3)
H1A—N1—H1C	109.5	C6—C7—C13	119.8 (2)
H1B—N1—H1C	109.5	C8—C7—C13	120.7 (2)
C1—O1—C9	115.4 (2)	C3—C8—C7	120.4 (2)
O2—C1—O1	124.9 (3)	C3—C8—C14	119.6 (2)
O2—C1—C3	124.9 (3)	C7—C8—C14	119.9 (2)
O1—C1—C3	110.2 (2)	O1—C9—H9A	109.5
O3—C2—O4	127.2 (3)	O1—C9—H9B	109.5
O3—C2—C4	116.1 (2)	H9A—C9—H9B	109.5
O4—C2—C4	116.6 (2)	O1—C9—H9C	109.5
C8—C3—C4	120.5 (2)	H9A—C9—H9C	109.5
C8—C3—C1	120.0 (2)	H9B—C9—H9C	109.5
C4—C3—C1	119.5 (2)	N1—C10—H10A	109.5
C5—C4—C3	118.3 (2)	N1—C10—H10B	109.5
C5—C4—C2	122.1 (2)	H10A—C10—H10B	109.5
C3—C4—C2	119.5 (2)	N1—C10—H10C	109.5
C6—C5—C4	121.3 (2)	H10A—C10—H10C	109.5
C6—C5—C11	119.5 (2)	H10B—C10—H10C	109.5
C4—C5—C11	119.2 (2)		
C9—O1—C1—O2	3.0 (5)	C2—C4—C5—C11	5.4 (4)
C9—O1—C1—C3	-177.0 (3)	C4—C5—C6—C7	0.2 (4)
O2—C1—C3—C8	63.3 (4)	C11—C5—C6—C7	177.8 (2)
O1—C1—C3—C8	-116.7 (3)	C4—C5—C6—C12	-179.9 (2)
O2—C1—C3—C4	-115.9 (3)	C11—C5—C6—C12	-2.3 (3)
O1—C1—C3—C4	64.1 (3)	C5—C6—C7—C8	-3.6 (4)
C8—C3—C4—C5	-3.9 (4)	C12—C6—C7—C8	176.5 (2)
C1—C3—C4—C5	175.3 (2)	C5—C6—C7—C13	176.6 (2)

C8—C3—C4—C2	176.6 (2)	C12—C6—C7—C13	-3.3 (3)
C1—C3—C4—C2	-4.2 (4)	C4—C3—C8—C7	0.6 (4)
O3—C2—C4—C5	-118.0 (3)	C1—C3—C8—C7	-178.6 (2)
O4—C2—C4—C5	63.7 (3)	C4—C3—C8—C14	-176.7 (2)
O3—C2—C4—C3	61.5 (3)	C1—C3—C8—C14	4.1 (3)
O4—C2—C4—C3	-116.8 (3)	C6—C7—C8—C3	3.2 (4)
C3—C4—C5—C6	3.5 (4)	C13—C7—C8—C3	-177.0 (2)
C2—C4—C5—C6	-177.0 (2)	C6—C7—C8—C14	-179.5 (2)
C3—C4—C5—C11	-174.1 (2)	C13—C7—C8—C14	0.3 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots O3 ⁱ	0.89	1.86	2.742 (3)	173
N1—H1B \cdots O4 ⁱⁱ	0.89	1.93	2.794 (3)	163
N1—H1C \cdots O4	0.89	1.92	2.797 (3)	170

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