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Hydrogen-bonded chains in 2,2,2-trichloro-*N*,*N*′-bis(4-methoxyphenyl)ethane-1,1-diamine and a three-dimensional hydrogen-bonded framework in 2,2,2-trichloro-*N*,*N*′-bis(4-chlorophenyl)ethane-1,1-diamine

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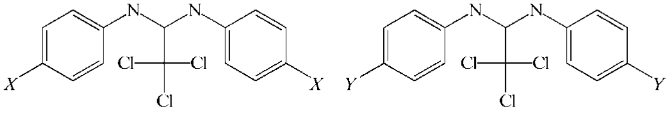
In 2,2,2-trichloro-*N*,*N*′-bis(4-methoxyphenyl)ethane-1,1-diamine, $C_{16}H_{17}Cl_3N_2O_2$, molecules are linked into helical chains by N—H···O hydrogen bonds. Molecules of 2,2,2-trichloro-*N*,*N*′-bis(4-chlorophenyl)ethane-1,1-diamine, $C_{14}H_{11}Cl_5N_2$, are connected into a three-dimensional framework by two independent Cl···Cl interactions and one C—H···Cl hydrogen bond.

Comment

As a continuation of our structural studies of bis(arylamino)trichloromethylmethanes (Zhang *et al.*, 2007), we report here the molecular and supramolecular structures of 2,2,2-trichloro-*N*,*N*′-bis(4-methoxyphenyl)ethane-1,1-diamine, (I) (Fig. 1), and 2,2,2-trichloro-*N*,*N*′-bis(4-chlorophenyl)ethane-1,1-diamine, (II) (Fig. 2), where the supramolecular aggregations prove to be different from those in 2,2,2-trichloro-*N*,*N*′-diphenylethane-1,1-diamine, (III), and 2,2,2-trichloro-*N*,*N*′-bis(4-methylphenyl)ethane-1,1-diamine, (IV),



(I) *X*=OMe
(II) *X*=Cl
(III) *Y*=H
(IV) *Y*=Me

which we reported recently (Zhang *et al.*, 2007). In (III), the two-dimensional supramolecular structure is built from C—H···Cl and C—H···π(arene) contacts, while the crystal structure of (IV) exhibits one-dimensional double columns formed by a combination of two independent C—H···Cl hydrogen bonds and one Cl···Cl interaction.

In compounds (I) and (II), the trichloroethane-1,1-diamine fragments adopt a *gauche* conformation with respect to the C1—C2 bonds, similar to the situation in (III) and (IV). In (II), the dihedral angle between the planes of the two aromatic rings is 88.01 (2)°, indicating that these benzene rings are perpendicular to one another. The orientation of the two rings is marginally different from that in (I), where the dihedral angle is 76.37 (3)°. Selected geometric parameters for (I) and (II) are listed in Tables 1 and 3, respectively. The C2—Cl1 bond in (I) is longer than the other C—Cl bonds in compounds (I)–(IV), probably due to the presence of an intramolecular N2—H2*D*···Cl1 hydrogen bond (Table 2). The same variation of *ca* 9° occurs within each pair of exocyclic C—C—O valence

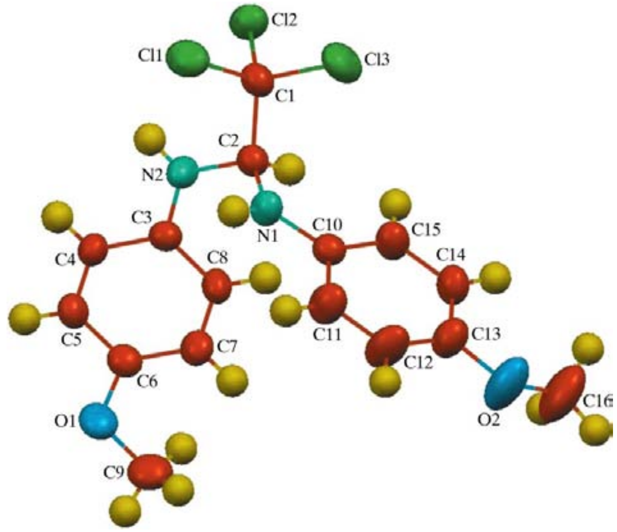


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

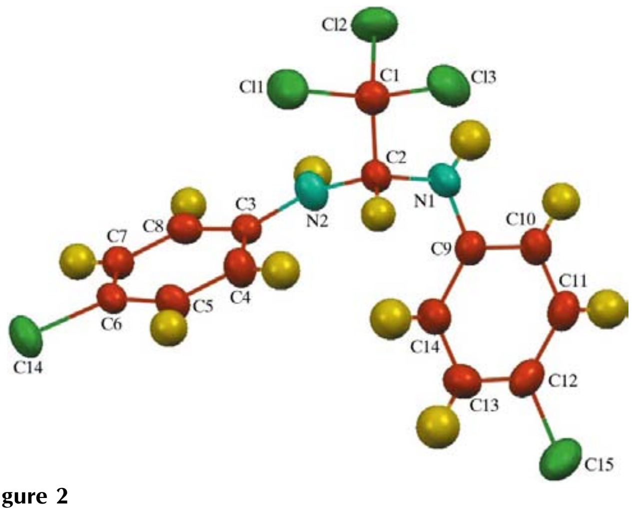


Figure 2
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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angles in (I), as is well established for 4-methoxyphenyl units (Seip & Seip, 1973). These deviations suggest the presence of repulsive interactions between O2—CH$_3$ and atom H14 (the distance between the methyl C atom and H14 is 2.61 Å) or O1—CH$_3$ and H7 (the distance between the methyl C atom and H7 is 2.55 Å). The methoxy group on C6 is effectively coplanar with the C3–C8 ring, as shown by the C7—C6—O1—C9 torsion angle of −4.3 (4)°. The situation is, however, different for the methoxy group on C13, where the torsion angle is −21.3 (5)° and the methyl C atom is displaced from the plane of the C10–C15 aryl ring by 0.408 (4) Å. In compound (II), the C1—N1—C9—C14 and C1—N2—C3—C4 torsion angles are −2.1 (3) and −9.5 (3)°, respectively, indicating that atom C1 lies near the N1/C9–C14 plane. However, atom C1 in (I) is displaced by 0.249 (3) and 0.265 (4) Å from the N2/C3–C8 and N1/C10–C15 planes, respectively.

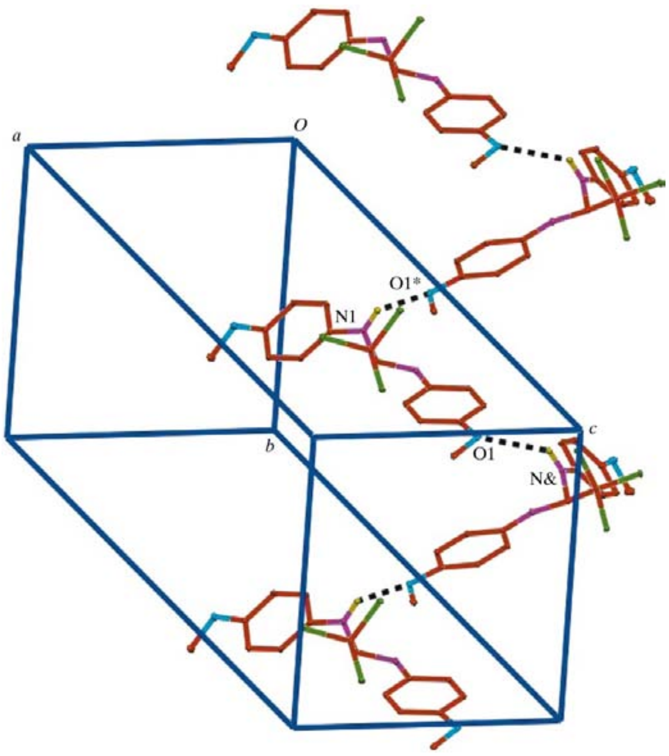

Figure 3
Part of the crystal structure of (I), showing the formation of a *C*(9) helical chain parallel to the [010] direction. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or ampersand (&) are at the symmetry positions $(-\frac{1}{2} - x, y - \frac{1}{2}, z)$ and $(-\frac{1}{2} - x, \frac{1}{2} + y, z)$, respectively.

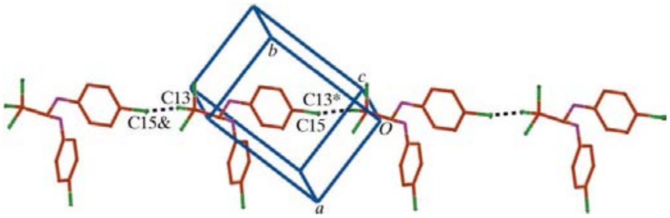

Figure 4
Part of the crystal structure of (II), showing the formation of a *C*(9) chain parallel to the [110] direction. Atoms marked with an asterisk (*) or ampersand (&) are at the symmetry positions $(x - 1, y - 1, z)$ and $(x + 1, y + 1, z)$, respectively.

The two NH H atoms in each molecule have very similar chemical shifts and coupling constants with the adjacent CH hydrogen [J = 8.8 Hz in (I) and 8.4 Hz in (II)], suggesting that, in solution at room temperature, on the NMR timescale, the molecules relax to a conformation where the two H—N—C—H torsion angles have similar average magnitudes, though the two H—N—C—H torsion angles in each molecule in the solid state are different [−169 and −128° for H1*D*—N1—C1—H1 and H2*D*—N2—C1—H1, respectively, in (I), and −155 and −128° for H2*D*—N2—C—H1 and H1*D*—N1—C1—H1, respectively, in (II)].

In compound (I), the molecules are linked into helical chains by a single N—H···O hydrogen bond (Table 2). Atom N1 in the molecule at (x, y, z) acts as a hydrogen-bond donor to methoxy atom O1 in the molecule at $(-\frac{1}{2} - x, y - \frac{1}{2}, z)$. Propagation by an *a*-glide plane at $x = -\frac{1}{4}$ then generates a *C*(9) (Bernstein *et al.*, 1995) chain running parallel to the [010] direction (Fig. 3). Eight chains of this type pass through each

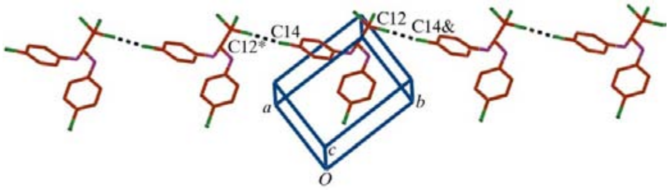

Figure 5
Part of the crystal structure of (II), showing the formation of a *C*(9) chain parallel to the $[1, y, \frac{1}{4}]$ direction. Atoms marked with an asterisk (*) or ampersand (&) are at the symmetry positions $(x + 1, y - 1, z)$ and $(x - 1, y + 1, z)$, respectively.

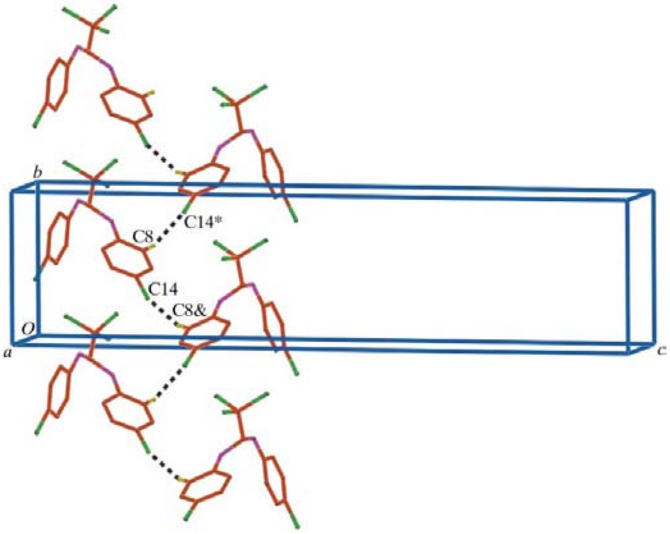

Figure 6
Part of the crystal structure of (II), showing the formation of a *C*(5) chain of rings along the [010] direction. Atoms marked with an asterisk (*) or ampersand (&) are at the symmetry positions $(2 - x, \frac{1}{2} + y, \frac{1}{2} - z)$ and $(2 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, respectively.

unit cell; four of these, running along the ($-\frac{1}{4}$, y, $\frac{3}{8}$), ($\frac{3}{4}$, y, $\frac{3}{8}$), ($-\frac{1}{4}$, y, $\frac{7}{8}$) and ($\frac{3}{4}$, y, $\frac{7}{8}$) directions, are related to each other by translational symmetry operations, and they are related by an a-glide plane to the other four chains running along the ($-\frac{1}{4}$, y, $\frac{1}{8}$), ($\frac{3}{4}$, y, $\frac{1}{8}$), ($-\frac{1}{4}$, y, $\frac{5}{8}$) and ($\frac{3}{4}$, y, $\frac{5}{8}$) directions. There are no direction-specific interactions between adjacent chains.

There are no aromatic π–π stacking interactions in the structure of (II); instead, the molecules are linked into a complex three-dimensional framework by a combination of two independent Cl$\cdots$Cl interactions and one C—H$\cdots$Cl hydrogen bond (Table 4). However, the structure of (II) can be easily analyzed in terms of three one-dimensional substrutures. In the first substructure, atom Cl5 in the molecule at (x, y, z) forms an intermolecular interaction with trichloromethyl atom Cl3 [Cl5$\cdots$Cl3 = 3.343 (2) Å] in the molecule at (x + 1, y, z). Propagation by translation then generates a C(9) chain running along the [110] direction (Fig. 4). In the same way, the second substructure is constructed by way of a Cl$\cdots$Cl interaction: atom Cl4 in the molecule at (x, y, z) forms another independent intermolecular interaction with trichloromethyl atom Cl2 [Cl4$\cdots$Cl2 = 3.469 (2) Å] in the molecule at ($x + 1, y - 1, z$), so forming by translation a C(9) chain parallel to the [$1\bar{1}0$] direction (Fig. 5). In the third substructure, atom H8 in the molecule at (x, y, z) acts as a hydrogen-bond donor to atom Cl4 in the molecule at ($-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$), thus generating a C(5) chain along the (1, y, $\frac{1}{4}$) direction and generated by a 2_1 screw axis along (1, y, $\frac{1}{4}$) (Fig. 6). The combination of these three chain motifs links molecules of (II) into a three-dimensional framework.

Experimental

For the synthesis of (I), chloral hydrate (16.5 g, 0.1 mol) and 4-methoxyaniline (0.2 mol) were mixed in ethyl acetate (25–30 ml) and heated until dissolution of the solid occurred. Cooling of the hot solution, followed by slow evaporation of the solvent at room temperature, yielded the crude product (yield 86%). Single crystals of (I) were obtained by recrystallization from CH_2Cl_2. ^{1}H NMR (DMSO, 400 MHz): δ 6.71 (m, 8H, 2Ar), 5.63 (d, J = 8.8 Hz, 2H, 2NH), 5.42 (t, J = 8.7 Hz, 1H, CH), 3.59 (s, 6H, $2CH_3$). Compound (II) was synthesized by heating with stirring a mixture of chloral hydrate (16.5 g, 0.1 mol), freshly distilled 4-chloroaniline (0.2 mol) and ethyl acetate (25–30 ml) until dissolution of the solid occurred. Cooling of the hot solution and slow evaporation of the solvent at room temperature yielded a crystalline product (yield 82%). Single crystals of (II) were obtained by recrystallization from hot dimethyl sulfoxide. ^{1}H NMR (DMSO, 400 MHz): δ 6.93 (m, 8H, 2Ar), 6.32 (d, J = 8.4 Hz, 2H, 2NH), 5.73 (t, J = 8.4 Hz, 1H, CH).

Compound (I)

Crystal data

$C_{16}H_{17}Cl_3N_2O_2$
M_r = 375.67
Orthorhombic, $Pbca$
a = 9.717 (2) Å
b = 10.575 (3) Å
c = 33.772 (8) Å

V = 3470.3 (14) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.54 mm^{-1}
T = 291 (2) K
0.38 × 0.29 × 0.25 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{\min}$ = 0.822, $T_{\max}$ = 0.876

23826 measured reflections
3233 independent reflections
2571 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.066

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.109
S = 1.05
3233 reflections

210 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.36 e Å^{-3}
$\Delta\rho_{\min}$ = −0.39 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cl1—C2	1.790 (3)	O2—C16	1.396 (4)
C10—N1—C1	125.2 (2)	O1—C6—C7	125.1 (2)
C3—N2—C1	121.8 (2)	C15—C10—N1	125.2 (2)
N1—C1—C2	111.4 (2)	C11—C10—N1	117.6 (2)
C8—C3—N2	123.6 (2)	C14—C13—O2	125.1 (3)
O1—C6—C5	115.8 (2)	O2—C13—C12	116.1 (3)
C3—N2—C1—N1	−67.7 (3)	C9—O1—C6—C7	−4.3 (4)
Cl3—C2—C1—N2	177.96 (18)	C1—N1—C10—C15	13.6 (4)
Cl2—C2—C1—N1	174.51 (18)	N1—C10—C11—C12	−179.6 (3)
C1—N2—C3—C8	−13.1 (4)	C11—C12—C13—O2	179.6 (3)
N2—C3—C4—C5	178.9 (2)		

Table 2
Hydrogen-bond and short-contact geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$D\cdots$Cl1	0.86	2.67	3.030 (3)	107
N1—H1$D\cdots$O1$^{\rm i}$	0.86	2.54	3.150 (3)	128

Symmetry code: (i) $-x - \frac{1}{2}, y - \frac{1}{2}, z$.

Compound (II)

Crystal data

$C_{14}H_{11}Cl_5N_2$
M_r = 384.50
Orthorhombic, $P2_12_12_1$
a = 6.0186 (6) Å
b = 8.0624 (8) Å
c = 33.082 (3) Å

V = 1605.3 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.90 mm^{-1}
T = 291 (2) K
0.42 × 0.31 × 0.28 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) $T_{\min}$ = 0.706, $T_{\max}$ = 0.791

11400 measured reflections
2990 independent reflections
2898 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.063
S = 1.03
2990 reflections
190 parameters
H-atom parameters constrained

$\Delta\rho_{\max}$ = 0.18 e Å^{-3}
$\Delta\rho_{\min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), with 607 Friedel pairs
Flack parameter: −0.02 (5)

Table 3
Selected geometric parameters (Å, °) for (II).

C9—C10	1.404 (3)		
C3—N2—C1	126.37 (16)	N1—C9—C14	123.45 (18)
N2—C3—C4	123.51 (17)		
C3—N2—C1—N1	144.05 (18)	C1—N1—C9—C14	−2.1 (3)
C1—N2—C3—C4	−9.5 (3)	N1—C9—C14—C13	179.2 (2)
N2—C3—C4—C5	177.69 (19)		

Table 4
Hydrogen-bond and short-contact geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*D*···Cl2	0.86	2.69	3.049 (2)	106
C8—H8···Cl4^{i}	0.93	2.89	3.774 (3)	160

Symmetry code: (i) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$.

H atoms were placed in idealized positions and allowed to ride on their respective parent atoms, with C—H = 0.98 Å and N—H = 0.86 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier atom).

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3036). Services for accessing these data are described at the back of the journal.

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