organic compounds

Two N,N′-diaryl-2,2,2-trichloro-ethane-1,1-diamines: hydrogen-bonded supramolecular structures in one and two dimensions

Zhen-Feng Zhang,[a]* **Dong-Chao Wang,**[a] **Jian-Ge Wang**[b] **and Gui-Rong Qu**[a]

[a]College of Chemistry and Environmental Science, Henan Normal University, Xinxiang 453007, People's Republic of China, and [b]College of Chemistry, Luoyang Normal University, Xinxiang 453007, People's Republic of China
Correspondence e-mail: zzf5188@sohu.com

The molecules of 2,2,2-trichloro-N,N′-diphenylethane-1,1-diamine, $C_{14}H_{13}Cl_3N_2$, are linked into (040) sheets by a combination of C—H···Cl and C—H···π(arene) hydrogen bonds. In 2,2,2-trichloro-N,N′-bis(4-methylphenyl)ethane-1,1-diamine, $C_{16}H_{17}Cl_3N_2$, the molecules are linked into $C(7)$ chains by two independent C—H···Cl hydrogen bonds and one Cl···Cl contact.

Comment

Some chloral derivatives with amides have found some use as hypnotics and sedatives as substitutes for chloral hydrate. However, chloral has been combined with amides to give only a few 'aldehyde ammonia'-type compounds for which therapeutic merit is claimed. In addition to the 'chloral amines', some bis(arylamino)trichloromethylmethanes have been prepared by condensing two molecules of aromatic primary amine with one molecule of chloral hydrate (Stumerford & Dalton, 1944).

Our interest in chloral derivatives with aromatic primary amines stems from their possible use as important intermediates in the construction of five-membered ring compounds (Katritzky & Fan, 1990). We have prepared several novel chloral derivatives. As part of our synthetic and structural studies, the structures of the title compounds, (I) and (II), have been determined.

The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. The trichloroethane-1,1-diamine fragments in the two molecules adopt a low-energy *gauche* conformation with respect to the C7—C14 and C8—C9 bonds, respectively. This is similar to the situation in analogous compounds containing the trichloromethyl group (Krishnaiah *et al.*, 2007; Hartung *et al.*, 2005). The two molecules adopt 'twist' conformations, with N1—C7—C14—Cl2 and N2—C7—C14—Cl2 torsion angles of −59.37 (2) and 65.57 (2)°,

respectively, for (I); the corresponding torsion angles, *viz.* N1—C8—C9—Cl3 and N2—C8—C9—Cl3, in (II) are

(I) X=H
(II) X=Mc
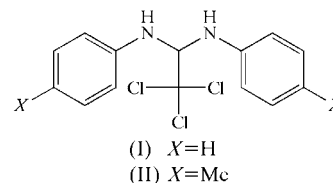
−63.52 (2) and 62.07 (2)°, respectively. In (I) and (II), the dihedral angles between the two aromatic rings are 87.2 (2) and 82.5 (1)°, respectively, indicating that the rings are almost perpendicular to one another (Figs. 1 and 2). The orientations are mainly attributed to a pair of intramolecular bifurcated donor hydrogen bonds (N1—H1D···Cl1 and N1—H1D···Cl2) for (I), and an intramolecular interaction (N2—H2D···Cl3) and a van der Waals repulsion effect between the trichloromethyl group and the two aromatic rings for (II) (Tables 2 and 4).
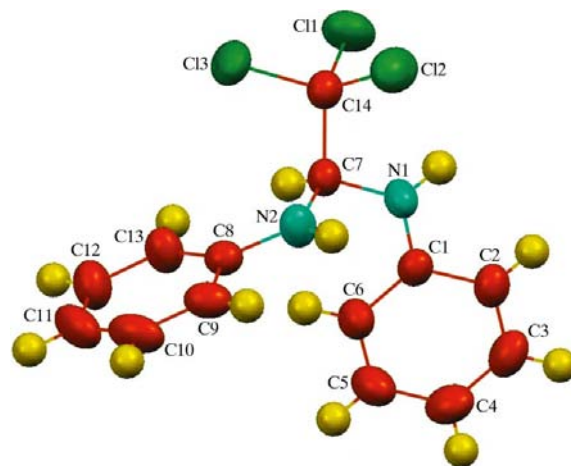

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.
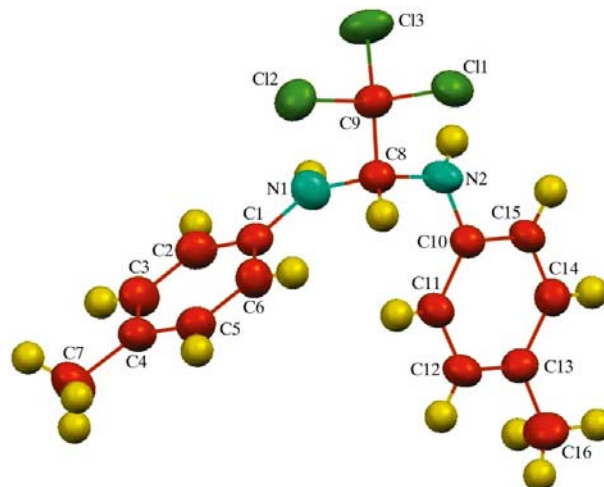

Figure 2
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Selected geometric parameters for the two molecules are given in Tables 1 and 3. The N1—C1 and N2—C8 distances in (I) and the corresponding N1—C1 and N2—C10 bond lengths in (II) are shorter than the standard N—C bond length (1.47 Å; Mak *et al.*, 2002). This is similar to what has been found in diphenylamine (Wang *et al.*, 2005). This difference is considered to be the result of π conjugation between the N atom and the aromatic ring. In (I), the C2—C1—N1—C7 and C9—C8—N2—C7 torsion angles (-177.2 and $-176.6°$, respectively) are consistent with the equivalent angles in (II) (-175.3 and $-6.2°$), showing that the N atoms lie approximately in the same plane as the aromatic rings to which they are bonded. However, compared with the ideal value of 120°, the C7—N2—C8 bond angle in (I) and the C1—N1—C8 angle in (II) are strikingly large. The deviation is due to a van der Waals repulsion between atoms H7 and H13 in (I), and between H6 and H8 in (II).

The two NH hydrogens in each molecule gave identical chemical shifts and coupling constants with the adjacent CH H atom [$J = 7.2$ Hz in (I) and 8.4 Hz in (II)], suggesting that in solution 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 [131.5 and 161.7° for H1D—N1—C7—H7 and H2D—N2—C7—H7, respectively, in (I), and 149.9 and 155.5° for H1D—N1—C8—H8 and H2D—N2—C8—H8, respectively, in (II)].

The molecules of (I) (Fig. 1) are linked into sheets by two hydrogen bonds, one of C—H···Cl and one of C—H···π(arene) type (Table 2), the formation of which is readily analyzed in terms of two one-dimensional substructures, one formed by the C—H···π hydrogen bond and one formed by the C—H···Cl hydrogen bond. For the sake of simplicity, we shall omit any further consideration of the C—H···C hydrogen bonds, which are too weak to influence the overall dimensionality of the supramolecular structure. In the first substructure, atom C9 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the C1–C6 ring in the molecule at $(x, -y + \frac{1}{2}, z - \frac{1}{2})$, thus forming a $C_2^2(8)$ chain running along the $(\frac{3}{4}, \frac{1}{4}, z)$ direction and generated by a 2_1 screw axis along $(\frac{3}{4}, \frac{1}{4}, z)$ (Fig. 3). In the second substructure, atom C4 in the molecule at (x, y, z) acts as a hydrogen-bond donor to trichloromethyl atom Cl3 in the molecule at $(x - 1, -y + \frac{1}{2}, z + \frac{1}{2})$, so forming a $C_2^2(9)$ chain running parallel to the $(\frac{1}{2}, 0, \frac{3}{4})$ direction and generated by a 2_1 screw axis along $(x, \frac{1}{4}, \frac{1}{2})$ (Fig. 4). The combination of the two chain motifs is sufficient to link all the molecules into a two-dimensional sheet parallel to (040) (Fig. 4). Two such sheets pass through each unit cell, in the domains $0 < y < \frac{1}{2}$ and $\frac{1}{2} < y < 1$.
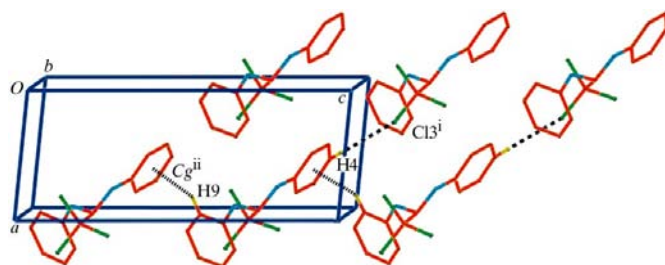

Figure 4
Part of the crystal structure of (I), viewed along the (010) direction, showing the formation of a (040) sheet. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Intermolecular interactions are represented by dashed lines. Selected atoms are labelled. [Symmetry codes: (i) $x - 1, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; Cg is the centroid of the C1–C6 ring.]
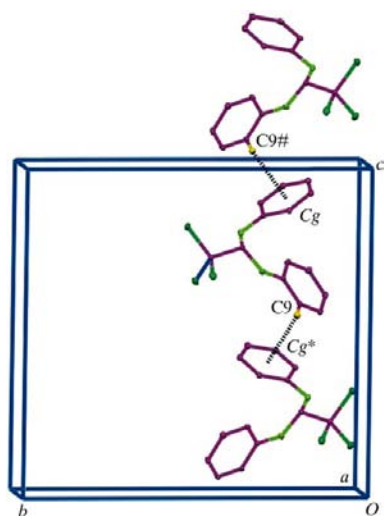

Figure 3
Part of the crystal structure of (I), showing the formation of a $C_2^2(8)$ chain along the $(\frac{3}{4}, \frac{1}{4}, y)$ direction. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, -y + \frac{1}{2}, z - \frac{1}{2})$ and $(x, -y + \frac{1}{2}, z + \frac{1}{2})$, respectively. ($Cg$ is the centroid of the C1–C6 ring.)
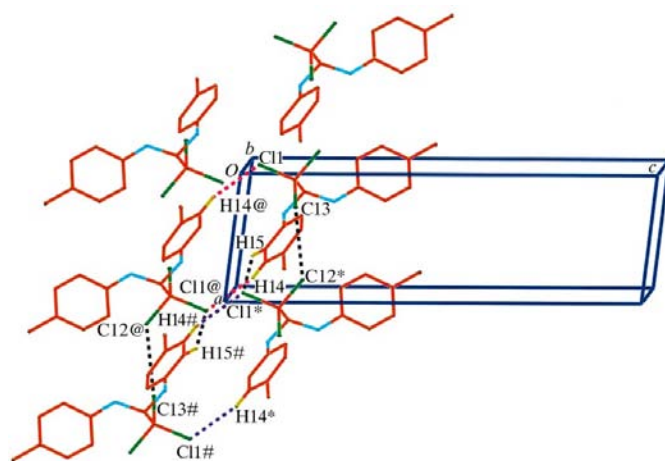

Figure 5
Part of the crystal structure of (II), showing the formation of an $R_2^2(16)$ dimer centred at $(\frac{1}{2}, 0, 0)$ and a $C(7)$ chain along the (100) direction. Atoms marked with an asterisk (*), a hash (#) or an 'at' symbol (@) are at the symmetry positions $(x + 1, y, z)$, $(-x + 2, -y, -z)$ and $(-x + 1, -y, -z)$, respectively.

organic compounds

The crystal structure of (II) takes on a simple one-dimensional double-columnar packing along the [100] direction *via* a combination of two independent C—H···Cl hydrogen bonds (Table 3) and one Cl···Cl interaction. Atom C14 in the molecule at (x, y, z) acts as a hydrogen-bond donor to trichloromethyl atom Cl1 in the molecule at $(-x + 1, -y, -z)$, so generating by inversion a dimer centred at $(\frac{1}{2}, 0, 0)$ and characterized by the usual $R_2^2(16)$ (Bernstein *et al.*, 1995) motif (Fig. 5). This dimer can be regarded as the backbone building unit within the structure, from which the one-dimensional double-columnar structure is built. The one-dimensional structure involves a C—H···Cl hydrogen bond and a Cl···Cl interaction. Atoms C15 and Cl3 in the molecule at (x, y, z), parts of the dimer centred at $(\frac{1}{2}, 0, 0)$, act as a hydrogen-bond donor and form an intermolecular contact, respectively, to trichloromethyl atoms Cl1 and Cl2 [Cl3···Cl2 = 3.491 (3) Å] in the molecule at $(x + 1, y, z)$, which is part of the dimer centred at $(\frac{3}{2}, 0, 0)$. Propagation by inversion then generates a $C(7)$ chain (Bernstein *et al.*, 1995) along the *a* axis.

There are no classical intermolecular hydrogen bonds present in either structure, though the NH groups could have taken on the role of active donor or acceptor groups in intermolecular interactions. The absence of classical hydrogen bonds can be attributed to steric control by the bulky groups nearby.

Experimental

Compound (I) was synthesized by heating, with stirring, a mixture of chloral hydrate (16.5 g, 0.1 mol), freshly distilled aniline (0.2 mol) and ethyl acetate (25–30 ml) until dissolution of the solid. Cooling of the hot solution and then slow evaporation of the solvent at room temperature yielded a crystalline product (yield 72%). Single crystals of (I) were obtained by recrystallization from ethyl acetate. ^{1}H NMR (DMSO, 400 MHz): δ 6.85 (*m*, 10H, 2Ar), 6.05 (*d*, J = 7.2 Hz, 2H, 2NH), 5.69 (*t*, J = 7.2 Hz, 1H, CH). For the synthesis of (II), chloral hydrate (33.1 g, 0.2 mol) was added at room temperature to a stirred solution of *p*-toluidine (43.2 g, 0.4 mol) in ethanol (40 ml). The mixture was then heated at about 323 K with stirring for 30 min. Natural cooling of the reaction mixture overnight gave a crystalline product, (II) (yield 25 g, 75%). Single crystals of (II) were obtained by recrystallization from ethyl acetate. ^{1}H NMR (DMSO, 400 MHz): δ 6.79 (*m*, 8H, $2C_6H_4$), 5.79 (*d*, J = 8.4 Hz, 2H, 2NH), 5.55 (*t*, J = 8.4 Hz, 1H, CH), 2.105 (*s*, 6H, $2CH_3$).

Compound (I)

Crystal data

$C_{14}H_{13}Cl_3N_2$	$V = 1458.4$ (3) Å^3
$M_r = 315.61$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 6.1225$ (7) Å	$\mu = 0.62$ mm^{-1}
$b = 15.7539$ (17) Å	$T = 291$ (2) K
$c = 15.2020$ (16) Å	$0.25 \times 0.17 \times 0.14$ mm
$\beta = 95.936$ (1)°	

Data collection

Bruker SMART CCD area-detector diffractometer	10979 measured reflections
	2717 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997*a*)	2041 reflections with $I > 2\sigma(I)$
$T_{min} = 0.863$, $T_{max} = 0.917$	$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	172 parameters
$wR(F^2) = 0.090$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{max} = 0.35$ e Å^{-3}
2717 reflections	$\Delta\rho_{min} = -0.34$ e Å^{-3}

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

Cl1—C14	1.768 (2)	N1—C1	1.393 (3)
Cl2—C14	1.774 (2)	N2—C8	1.392 (3)
Cl3—C14	1.761 (2)		
C1—N1—C7	122.18 (19)	N2—C7—C14	112.18 (18)
C8—N2—C7	126.77 (19)	C7—C14—Cl1	110.68 (16)
N2—C7—N1	112.50 (18)	C7—C14—Cl2	111.44 (15)

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

Cg is the centroid of the C1–C6 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1D···Cl2	0.86	2.69	3.055 (2)	107
N1—H1D···Cl1	0.86	2.89	3.049 (2)	92
C4—H4···Cl3^i	0.93	2.94	3.755 (3)	147
C9—H9···Cg^{ii}	0.93	2.74	3.547 (3)	145

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

Compound (II)

Crystal data

$C_{16}H_{17}Cl_3N_2$	$V = 1641.2$ (3) Å^3
$M_r = 343.67$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 5.9238$ (7) Å	$\mu = 0.55$ mm^{-1}
$b = 14.6193$ (16) Å	$T = 291$ (2) K
$c = 19.093$ (2) Å	$0.44 \times 0.35 \times 0.26$ mm
$\beta = 96.992$ (1)°	

Data collection

Bruker SMART CCD area-detector diffractometer	11838 measured reflections
	3756 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997*a*)	2955 reflections with $I > 2\sigma(I)$
$T_{min} = 0.793$, $T_{max} = 0.871$	$R_{int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.099$	
$S = 1.03$	
3756 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
200 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}

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

Cl1—C9	1.773 (2)	N1—H1D	0.81 (2)
Cl2—C9	1.7661 (19)	N2—C10	1.406 (2)
Cl3—C9	1.7770 (18)	N2—C8	1.437 (2)
N1—C1	1.400 (2)	N2—H2D	0.76 (2)
N1—C8	1.438 (2)	C8—C9	1.557 (2)
C1—N1—C8	125.76 (16)	C2—C1—N1	118.62 (16)
C1—N1—H1D	116.1 (16)	C6—C1—N1	123.87 (17)
C8—N1—H1D	116.1 (16)	N2—C8—N1	114.08 (15)
C10—N2—C8	121.48 (16)	N2—C8—C9	108.01 (15)
C10—N2—H2D	115.7 (18)	N1—C8—C9	110.73 (15)
C8—N2—H2D	116.4 (18)	C15—C10—N2	118.22 (16)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$D\cdots$Cl3	0.76 (2)	2.70 (2)	3.085 (2)	113 (2)
C14—H14$\cdots$Cl1[i]	0.93	2.93	3.699 (2)	141
C15—H15$\cdots$Cl1[ii]	0.93	2.88	3.705 (3)	148

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

H atoms in (I) were placed in idealized positions and allowed to ride on their respective parent atoms, with C—H distances of 0.93–0.98 Å and N—H distances of 0.86 Å, and with U_{iso}(H) values of $1.2U_{eq}$(C,N). In (II), H atoms bonded to N atoms were refined with an N—H distance restraint of 0.87 (2) Å, and with U_{iso}(H) values of $1.2U_{eq}$(N). Other H atoms were positioned geometrically and allowed to ride on their respective parent atoms, with C—H distances of 0.93–0.98 Å and with U_{iso}(H) values of 1.2 (1.5 for methyl groups) times U_{eq}(C).

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

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Hartung, J., Schmidt, P., Svoboda, I. & Fuess, H. (2005). *Acta Cryst.* E**61**, o1736–o1737.

Katritzky, A. R. & Fan, W. Q. (1990). *J. Org. Chem.* **55**, 3205–3213.

Krishnaiah, M., Radha Krishna, J., Jagadeesh Kumar, N., Devandranath Reddy, C. & Rao, S. N. (2007). *Acta Cryst.* E**63**, o731–o732.

Mak, T. C. W., Zhou, G. D. & Li, W. K. (2002). *Advanced Inorganic Structural Chemistry*. Beijing University Press and Chinese University of Hong Kong Press.

Sheldrick, G. M. (1997a). *SADABS, SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (1997b). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Stumerford, W. T. & Dalton, D. N. (1944). *J. Org. Chem.* **9**, 81–84.

Wang, S.-Q., Zhang, Z.-F., Wang, X., Huang, M.-Y. & Jiang, Y.-Y. (2005). *Acta Cryst.* E**61**, o1872–o1874.