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1,1′-(Ethenylidene)bis(4-chlorobenzene)

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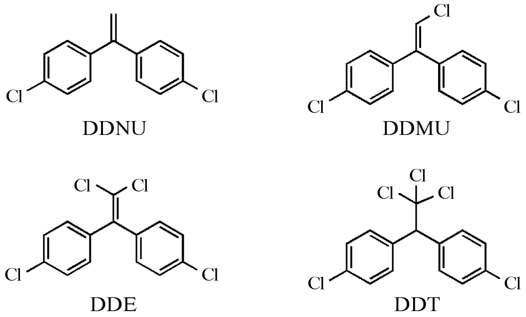
The title compound, $C_{14}H_{10}Cl_2$, crystallizes as colourless prisms with two symmetry-independent molecules in the unit cell. Numerous intermolecular C—H$\cdots\pi$ interactions dominate in the crystal structure, where C—H$\cdots$Cl and long Cl$\cdots$Cl contacts are also observed.

Comment

1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) has been recognized as one of the most problematic persistent organic pollutants (POPs). These compounds are relatively recent in origin, dating to the boom in industrial production after World War II. It has been found that DDT causes serious health and developmental problems in humans and wildlife even at low concentrations (Fellenberg, 2000). Therefore, extensive studies have been carried out using several methods for the degradation of DDT (Alonso *et al.*, 2002; Häggblom & Bossert, 2003). Recently, the partial electrochemical dechlorination of DDT mediated by a hydrophobic cobalamin derivative (hydrophobic vitamin B_{12}) yielded various dechlorinated products, such as 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (DDD), 1,1-bis(4-chlorophenyl)-2,2-dichloroethylene (DDE), 1,1,4,4-tetrakis(4-chlorophenyl)-2,3-dichloro-2-butene (TTDB) and 1-chloro-2,2-bis(4-chlorophenyl)ethylene (DDMU) (Shimakoshi, Tokunaga & Hisaeda, 2004). Structural data for DDD, DDE and DDMU have been reported from the viewpoint of toxicity (Shields *et al.*, 1977; Kennard *et al.*, 1984). We have also reported the crystal structure and geometry of (*E*)-TTDB (Shimakoshi, Aritome *et al.* 2004) and (*Z*)-TTDB (Shimakoshi *et al.*, 2005). With increasing environmental concern, it is imperative that new environmentally friendly approaches for the dechlorination of DDT be developed. To achieve this, DDT was dechlorinated in an ionic liquid system, 1-butyl-3-methylimidazolium tetrafluoroborate, or [bmim]BF_4, and the title compound, 1,1′-(ethenylidene)bis(4-chlorobenzene), DDNU, was obtained as one of the dechlorinated products. The ionic liquid system was explained briefly by Sheldon (2001) and Welton (1999). In this paper, the crystal structure of DDNU is reported in comparison with those of DDT and its metabolites.



DDNU crystallizes as colourless prisms with two symmetry-independent molecules, denoted 1 and 2, in the asymmetric unit (Fig. 1). The two independent molecules are an approximate inverted image of each other, although the aryl rings cannot be superimposed exactly. The dihedral angles between the two aryl planes are 63.59 (11) and 63.86 (10)° for molecules 1 and 2, respectively, and the aryl rings are not related by symmetry, while in DDT and its analogues there is mirror symmetry between the two aryl rings. The butterfly configuration of DDNU is distorted compared with that of DDT (DeLacy & Kennard, 1972) and its metabolites. The absence of Cl atoms at the terminal C atom, as well as the presence of Cl$\cdots$Cl short contacts, might be responsible for this distortion compared with DDT and its congeners. Therefore, the unit-cell parameters of DDNU are also different. The unit-cell parameters of DDNU, DDMU, DDE and DDT are compared in Table 1. The C—C bond distances to the terminal C atom of DDNU are also different from those in DDT and its related compounds (Table 2).

In the crystal structure of DDNU, numerous intermolecular C—H$\cdots\pi$ interactions dominate in the crystal structure and

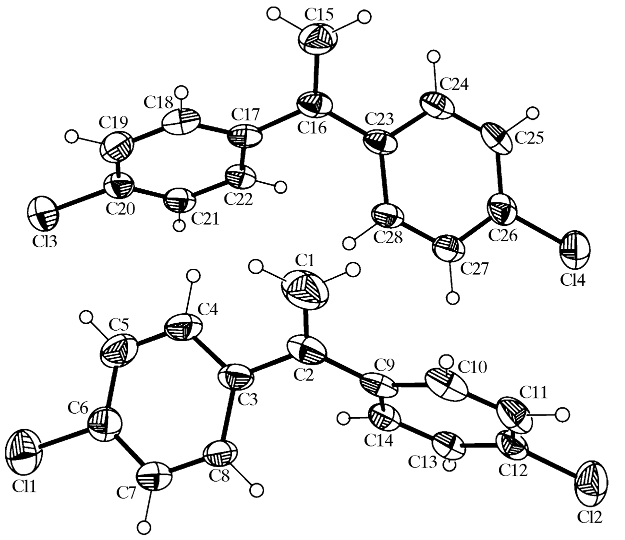


Figure 1
The two crystallographically independent molecules of DDNU in the asymmetric unit, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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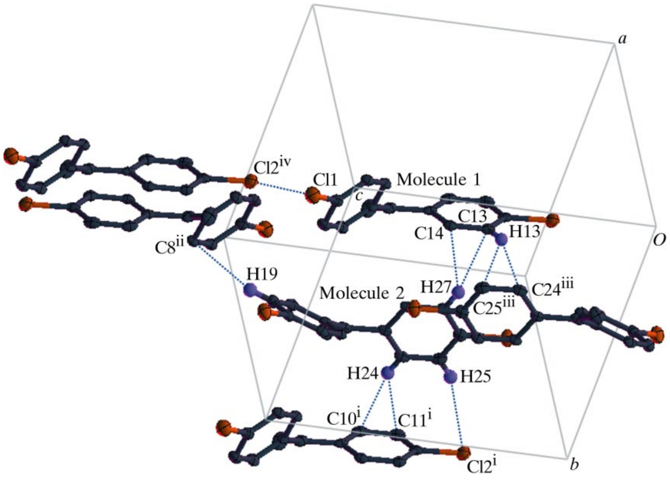

Figure 2
A view of the partial packing of DDNU, showing C—H$\cdots\pi$, C—H$\cdots$Cl and Cl$\cdots$Cl interactions as dashed lines. Only H atoms involved in these interactions are shown. [Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, -y+1, -z+2$; (iii) $-x, -y+1, -z+1$; (iv) $x, y, z+1$.]

long Cl$\cdots$Cl contacts are also observed. Additionally, there is a C25—H25$\cdots$Cl2($x, y+1, z$) contact of 3.798 (3) Å, with the C25—H25$\cdots$Cl2 angle being 151°. These contacts may be characterized as weak electrostatic interactions rather than weak hydrogen bonds (Bats *et al.*, 2001). A partial packing view of the crystal organization of DDNU showing C—H$\cdots\pi$, C—H$\cdots$Cl and weak Cl$\cdots$Cl short contacts is presented in Fig. 2, and details of four distinct C—H$\cdots\pi$ interactions between the two independent molecules of DDNU in the asymmetric unit are given in Table 3.

A Cl1$\cdots$Cl2($x, y, z+1$) interaction of 3.4432 (13) Å in the symmetric units of two DDNU molecules is also observed. The intermolecular Cl$\cdots$Cl short contact distance is less than the sum of the van der Waals radii (3.50 Å; Bondi, 1964). It has been reported (Gavezzotti & Filippini, 1993; Rowland & Taylor, 1996; Cox *et al.*, 1997) in many halogen-containing crystal structures in the Cambridge Structural Database (CSD, Version 5.25; Allen, 2002) that a significant number of Cl$\cdots$Cl non-bonded contacts of less than 3.5 Å have been observed. It has been suggested (Pedireddi *et al.*, 1994) that polarization and anisotropic electron distribution are important factors in the formation of these short contacts. This may be one of the reasons for the difference in the C—C bond length on the terminal C atom of the ethylene unit between DDE and DDNU. Successive Cl substituents at the terminal C atom appear to alter significantly the torsion angles between DDNU, DDMU and DDE, and these are compared in Table 4.

Experimental

The title compound, DDNU, was obtained from the electrolysis of DDT in the ionic liquid system of 1-butyl-3-methylimidazolium tetrafluoroborate, or [bmim]BF$_4$, with a carbon felt electrode (CFE) (area 3 × 1 cm) containing a catalytic amount of a hydrophobic vitamin B$_{12}$ derivative at an applied potential of −1.5 V *versus* Ag/AgCl. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of DDNU in chloroform–ethanol (1:1 *v*/*v*) as colourless prisms within 3–4 d.

Crystal data

$C_{14}H_{10}Cl_2$
$M_r = 249.12$
Triclinic, $P\overline{1}$
$a = 9.715$ (2) Å
$b = 9.745$ (2) Å
$c = 13.868$ (2) Å
$\alpha = 91.210$ (4)°
$\beta = 102.457$ (3)°
$\gamma = 108.561$ (4)°
$V = 1209.6$ (4) Å^3
$Z = 4$
$D_x = 1.368$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.50$ mm^{-1}
$T = 173$ (2) K
Prism, colourless
0.25 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.884$, $T_{max} = 0.951$
7314 measured reflections
4553 independent reflections
2835 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 25.7°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.155$
$S = 1.00$
4553 reflections
289 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0845P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

H atoms were located in geometric positions (C—H = 0.94–0.98 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C). The residual electron-density map contained small peaks of electron density (*ca* 0.53 e Å^{-3}) in the vicinity of atom Cl2.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

Table 1
Comparison of unit-cell parameters of DDNU, DDMU, DDE and DDT.

Parameter	DDNU[a]	DDMU[b]	DDE[c]	DDT[d]
a (Å)	9.715 (2)	15.163 (7)	9.219 (1)	9.963 (1)
b (Å)	9.745 (2)	5.824 (2)	35.496 (5)	19.200 (2)
c (Å)	13.868 (2)	7.452 (3)	9.438 (1)	7.887 (1)
α (°)	91.210 (4)			
β (°)	102.457 (3)	100.12 (3)	114.70 (1)	
γ (°)	108.561 (4)			
V (Å^3)	1209	648	3088	1509
Space group	$P\overline{1}$	$P2_1$	$P2_1/c$	$Pca2_1$

References: (*a*) this work; (*b*) Kennard *et al.* (1984); (*c*) Shields *et al.* (1977); (*d*) DeLacy & Kennard (1972).

Table 2
Comparison of selected bond lengths (Å) at the terminal C atom between DDNU, DDMU, DDE and DDT.

Bond	DDNU[a]	DDMU[b]	DDE[c]	DDT[d]
C1—C2	1.339 (5)	1.296 (1)	1.320 (1)	1.540 (4)
C15—C16	1.342 (4)		1.322 (1)	
C2—C3	1.483 (4)	1.483	1.487 (9)	1.531 (4)
C16—C17	1.492 (4)		1.491 (9)	
C2—C9	1.477 (4)	1.515 (8)	1.492 (1)	1.522 (8)
C16—C23	1.476 (4)		1.471 (1)	

References: (*a*) this work; (*b*) Kennard *et al.* (1984); (*c*) Shields *et al.* (1977); (*d*) DeLacy & Kennard (1972).

Table 3
Geometry of C—H···π interactions (Å, °) for DDNU.

*Cg*1, *Cg*2 and *Cg*3 are the centroids of rings C9–C14, C3–C8 and C23–C28, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C27—H27···*Cg*1	0.95	2.918	3.676	137
C24—H24···*Cg*1^{i}	0.95	2.793	3.599	143
C19—H19···*Cg*2^{ii}	0.95	2.897	3.614	133
C13—H13···*Cg*3^{iii}	0.95	3.063	3.773	132

Symmetry codes: (i) $x, y + 1, z$; (ii) $1 - x, 1 - y, 2 - z$; (iii) $-x, 1 - y, 1 - z$.

Table 4
Comparison of selected torsion angles (°) for DDNU, DDMU and DDE.

Angle	DDNU[a]	DDMU[b]	DDE[c]
C1—C2—C9—C14	−152.18 (3)	104.0 (1)	127.0 (1)
C1—C2—C3—C8	−135.39 (4)	−38.0 (1)	−52.0 (1)
C15—C16—C17—C22	148.70 (3)		121.0 (1)
C15—C16—C23—C28	138.30 (4)		−48.3 (1)

References: (*a*) this work; (*b*) Kennard *et al.* (1984); (*c*) Shields *et al.* (1977).

SHELXTL (Bruker, 2001); 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: GZ3023). Services for accessing these data are described at the back of the journal.

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