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Syntheses, crystal structures and Hirshfeld surface analyses of (*E*)-1-[2,2-dichloro-1-(2,3-dimethoxyphenyl)ethen-1-yl]-2-phenyldiazene and (*E*)-1-(4-chlorophenyl)-2-[2,2-dichloro-1-(2,3-dimethoxyphenyl)ethen-1-yl]diazene

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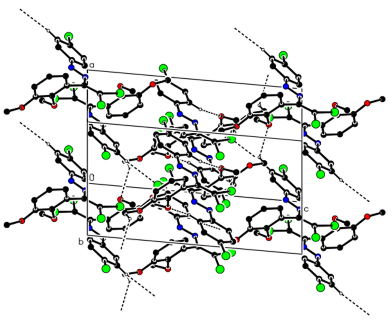
The crystal structures and Hirshfeld surface analyses of two similar azo compounds are reported. (*E*)-1-[2,2-dichloro-1-(2,3-dimethoxyphenyl)ethen-1-yl]-2-phenyldiazene, $C_{16}H_{14}Cl_2N_2O_2$, (**I**), crystallizes in space group $P2_1/c$ with Z = 4, and (*E*)-1-(4-chlorophenyl)-2-[2,2-dichloro-1-(2,3-dimethoxyphenyl)ethen-1-yl]diazene, $C_{16}H_{13}Cl_3N_2O_2$, (**II**), in the space group $P\overline{1}$ with Z = 4. In the crystal structure of (**I**), the molecules form layers parallel to the (010) plane through C—H$\cdots\pi$ and C—Cl$\cdots\pi$ interactions and van der Waals interactions between these layers consolidate the packing. There are two symmetry-independent molecules in the asymmetric unit of (**II**). In the crystal, molecules are connected by C—H$\cdots$O and C—H$\cdots$Cl hydrogen bonds, forming a three-dimensional network. C—Cl$\cdots\pi$ interactions also contribute to the packing. The intermolecular contacts in the crystals (**I**) and (**II**) were analysed using Hirshfeld surface analysis and two-dimensional fingerprint plots.



1. Chemical context

Azo dyes continue to attract considerable attention due to their wide applications in the textile (O'Neill *et al.*, 2000; Garg *et al.*, 2017), optical (Al-Mudhaffer *et al.*, 2016; Mohr & Wolfbeis, 1994), and biological fields (Khan *et al.*, 2021; Singh & Singh, 2017). The presence of functional groups in the obtained compounds provides broad opportunities for further chemical transformations and structural modifications. In this paper, we report the synthesis of two new dichlorodiazadienes, namely (*E*)-1-[2,2-dichloro-1-(2,3-dimethoxyphenyl)ethen-1-yl]-2-phenyldiazene, $C_{16}H_{14}Cl_2N_2O_2$, (**I**), and (*E*)-1-(4-chlorophenyl)-2-[2,2-dichloro-1-(2,3-dimethoxyphenyl)ethen-1-yl]diazene, $C_{16}H_{13}Cl_3N_2O_2$, (**II**). These compounds were synthesized in two steps starting from 2,3-dimethoxybenzaldehyde and phenylhydrazine and its chloro-substituted derivative. In the first step, the corresponding Schiff bases were obtained by condensation in ethanol under reflux in the presence of acetic acid. In the second step, the resulting hydrazones were converted into the target azo dyes by reaction with carbon tetrachloride in DMSO at room temperature

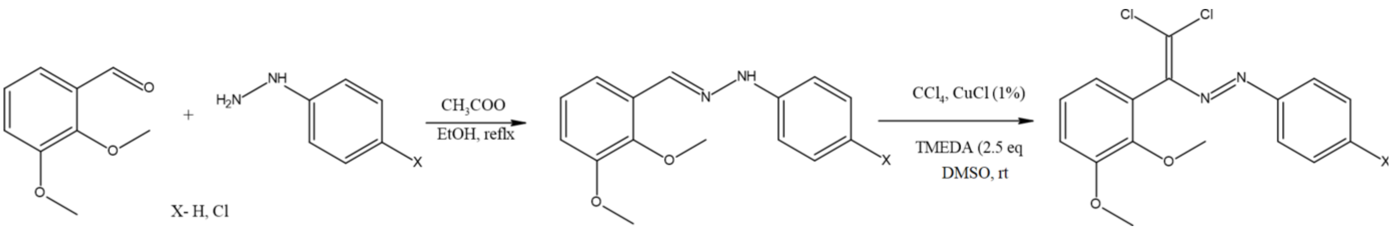
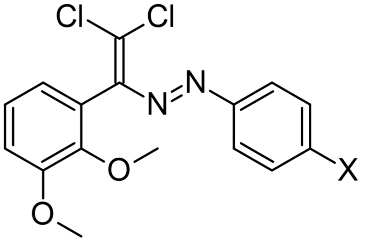


Figure 1
Reaction scheme for compounds (**I**) and (**II**).

in the presence of a $CuCl_2$ catalyst and tetramethylethylenediamine (TMEDA) (Fig. 1).

The formation of a dichloroethenyl fragment and an azo (–N═N–) chromophore within the same molecular system significantly enhances the functional diversity of the synthesized compounds. Such structural features not only affect their electronic and optical properties, but also enable their participation in various intermolecular interactions in the solid state. Therefore, in addition to the synthesis, detailed single-crystal X-ray diffraction and Hirshfeld surface analyses were performed to investigate the molecular and supramolecular structures of compounds (**I**) and (**II**).



(**I**) : X = H, (**II**) : X = Cl

2. Structural commentary

The central molecular fragment of (**I**), C1/C2/N1/N2/C3/C11/Cl1/Cl2, is almost planar (Fig. 2), with a root-mean-square (r.m.s.) deviation of fitted atoms from the least-squares plane of 0.0304 Å. This plane forms dihedral angles of 80.8 (1) and 26.7 (1) °, respectively, with the planes of the C3–C8 and C11–C16 benzene rings. The conformation of molecule (**I**) may be consolidated by a short C—H⋯O contact (Table 1, Fig. 2), forming an *S*(6) motif.

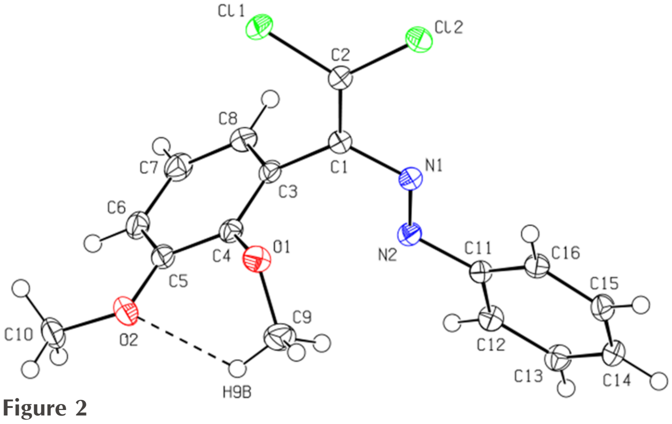


Figure 2
The molecular structure of (**I**), showing the atom labelling and displacement ellipsoids drawn at the 50% probability level. The short contact is indicated by a dashed line.

There are two symmetry-independent molecules, *A* (containing N1) and *B* (containing N3), in the asymmetric unit of (**II**) (Fig. 3). An overlay fit of inverted molecule *B* on molecule *A* is shown in Fig. 4, the weighted r.m.s. fit of the 17

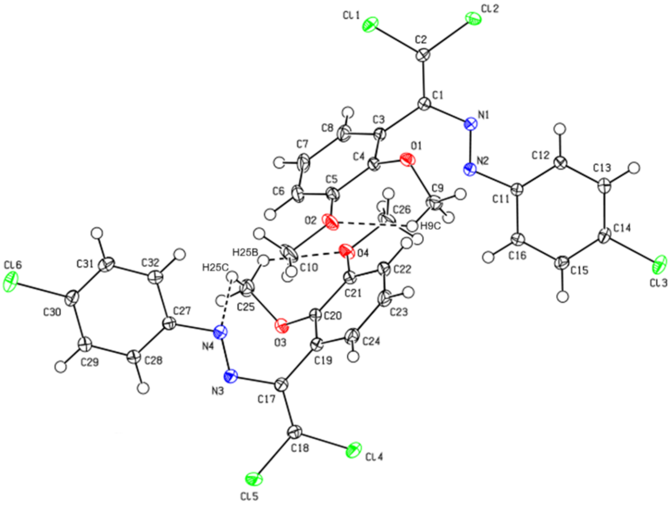


Figure 3
The molecular structure of (**II**), showing the atom labelling and displacement ellipsoids drawn at the 50% probability level. Hydrogen bonds are indicated by dashed lines.

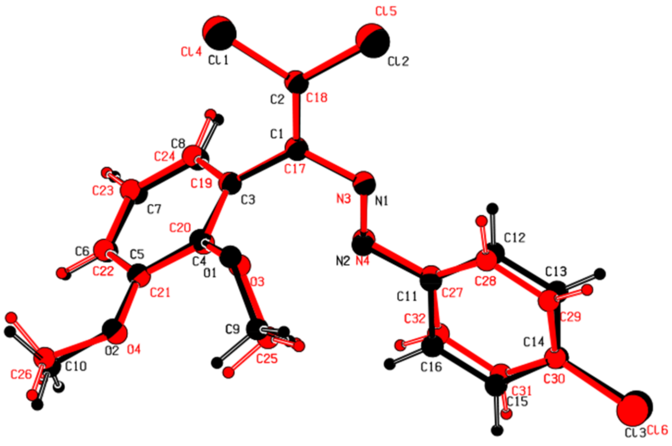


Figure 4
A least-squares overlay of the two independent molecules *A* and *B* of (II) [inverted molecule *B* (red) on molecule *A* (black)].

Table 1
Hydrogen-bond geometry (Å, °) for (**I**).

Cg and *Cg*2 are the centroids of the C3–C8 and C11–C16 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*B*···O2	0.98	2.35	2.955 (2)	119
C8—H8···$Cg2^{\rm i}$	0.95	2.52	3.4665 (16)	174
C10—H10*A*···$Cg1^{\rm ii}$	0.98	2.77	3.6231 (18)	146

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*C*···O2	0.98	2.32	2.9059 (12)	117
C10—H10*C*···$O3^{\rm i}$	0.98	2.65	3.3241 (13)	126
C12—H12···$O1^{\rm ii}$	0.95	2.66	3.2919 (11)	125
C25—H25*B*···O4	0.98	2.33	2.9226 (12)	118
C25—H25*C*···N4	0.98	2.58	3.2210 (13)	124
C31—H31···$Cl2^{\rm iii}$	0.95	2.87	3.7991 (10)	166

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

non-H atoms being 0.200 Å and showing the differences to be in the chlorophenyl groups C11–C16 and C27–C32. The central molecular fragment of molecule *A*, C1/C2/N2/N1/C3/C11/Cl1/Cl2, is also close to planar with an r.m.s. deviation of fitted atoms of 0.0226 Å (Fig. 3) and makes dihedral angles of 72.9 (1) and 6.6 (1)°, respectively, with the planes of the C3–C8 and C11–C16 benzene rings. The central molecular fragment of molecule *B*, C17/C18/N3/N4/C19/C27/Cl4/Cl5, is likewise almost planar with an r.m.s. deviation of fitted atoms of 0.0472 Å (Fig. 3) and makes dihedral angles of 69.1 (1) and 22.7 (1)°, respectively, with the planes of the (C19–C24) and (C27–C32) benzene rings. The conformation of molecule *A* features an intramolecular C—H···O hydrogen bond forming an *S*(6) motif, while the conformation of molecule *B* features intramolecular C—H···O and C—H···N hydrogen bonds (Table 2), which form *S*(6) and *S*(8) motifs, respectively.

3. Supramolecular features and Hirshfeld surface analyses

In the crystal structure of (**I**), the molecules form layers parallel to the (020) plane through C—H···π and C—Cl···π interactions [C2—Cl2···$Cg2^{a}$: C2—Cl2 = 1.7131 (15) Å, Cl2···$Cg2^{a}$ = 3.9882 (7) Å, C2···$Cg2^{a}$ = 4.2031 (16) Å, C2—Cl2···$Cg2^{a}$ = 85.07 (5)°, Symmetry code: (*a*) *x*, *y*, 1 + *z*; where *Cg*2 is the centroid of the (C11–C16) benzene ring] (Table 1, Figs. 5 and 6). van der Waals interactions between these layers consolidate the packing.

In the crystal of (**II**), the molecules are connected by C—H···O and C—H···Cl hydrogen bonds, forming a three-dimensional network (Table 2, Figs. 7 and 8). Additionally, C—Cl···π interactions [C2—Cl2···$Cg2^{b}$: C2—Cl2 = 1.7149 (9) Å, Cl2···$Cg2^{b}$ = 3.4334 (7) Å, C2···$Cg2^{b}$ = 3.7761 (11) Å, C2—Cl2···$Cg2^{b}$ = 87.72 (3), and C18—Cl5···$Cg4^{c}$: C18—Cl5 = 1.7159 (9) Å, Cl5···$Cg4^{c}$ = 3.8775 (7) Å, C18···$Cg4^{c}$ = 4.1527 (13) Å, C18—Cl5···$Cg4^{c}$ = 86.84 (4)°, Symmetry codes: (*b*) 1 − *x*, −*y*, 1 − *z*; (c) 2 − *x*, 1 − *y*, −*z*; where *Cg*2 and *Cg*4 are the centroids of the chlorophenyl rings (C11–C16 and C27–C32) of molecules *A* and *B*, respectively] also contribute to the packing.

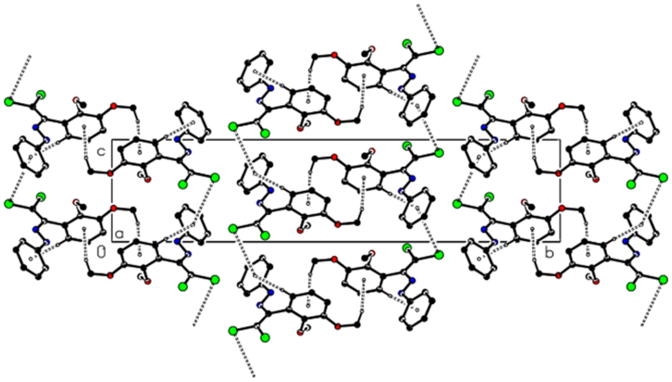


Figure 5
View of the C—H···π and C—Cl···π interactions of (**I**) along the *a* axis. H atoms not involved in hydrogen bonding were removed for clarity.

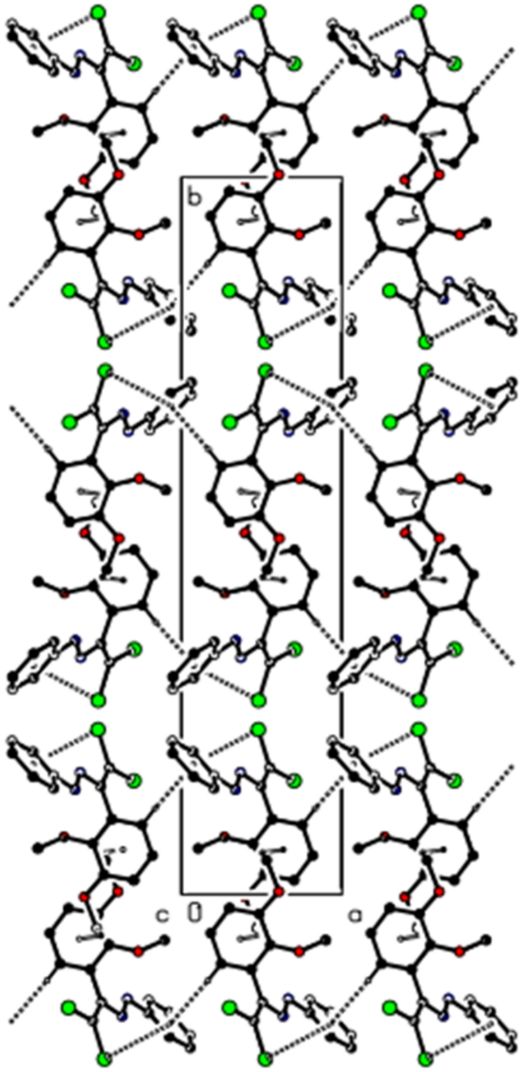


Figure 6
View of the C—H···π and C—Cl···π interactions of (**I**) along the *c* axis. H atoms not involved in hydrogen bonding were removed for clarity.

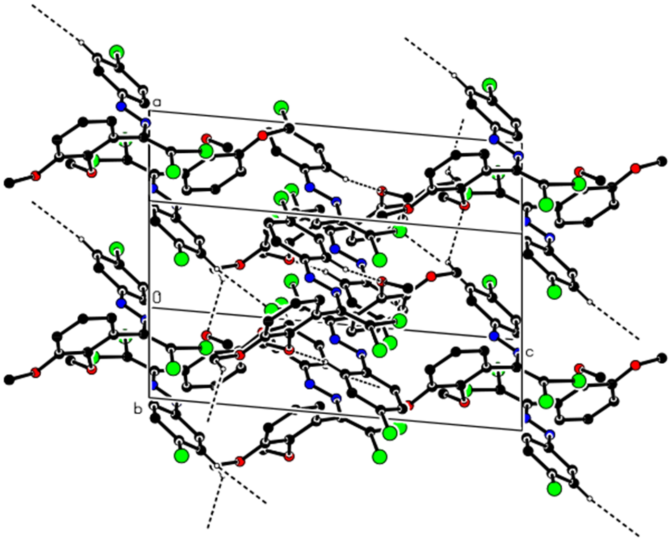


Figure 7
View of the C—H···O and C—H—Cl interactions (**II**) along the *b* axis. H atoms not involved in hydrogen bonding were removed for clarity.

Crystal Explorer 17.5 (Spackman *et al.*, 2021) was used to generate Hirshfeld surfaces in the crystal structures of (**I**) and (**II**). The $d_{\rm norm}$ mappings for (**I**) and molecules *A* and *B* of (**II**) were performed in the ranges −0.12 to 1.21 a.u., −0.10 to 1.35 a.u. and −0.10 to 1.66 a.u., respectively. The C···H/H···C, Cl···H/H···Cl and O···H/H···O interactions are indicated by red areas on the Hirshfeld surfaces (Fig. 9*a* for (**I**) and Fig. 9*c*,*d* for molecules *A* and *B* of (**II**). The two-dimensional fingerprint plots are shown in Fig. 10. The dominant interactions in the crystal packing of the title compounds are H···H [(**I**): 35.9%, (**II**) *A*: 29.6% and (**II**) *B*: 28.2%], C···H/H···C [(**I**): 21.1%, (**II**) *A*: 13.6% and (**II**) *B*: 12.0%], Cl···H/H···Cl [(**I**): 20.2%, (**II**) *A*: 29.1% and (**II**) *B*: 31.3%], O···H/H···O [(**I**): 7.6%, (**II**) *A*: 7.5% and (**II**) *B*: 7.1%]. The presence of different functional groups in the compounds leads to some differences in the remaining weak interactions.

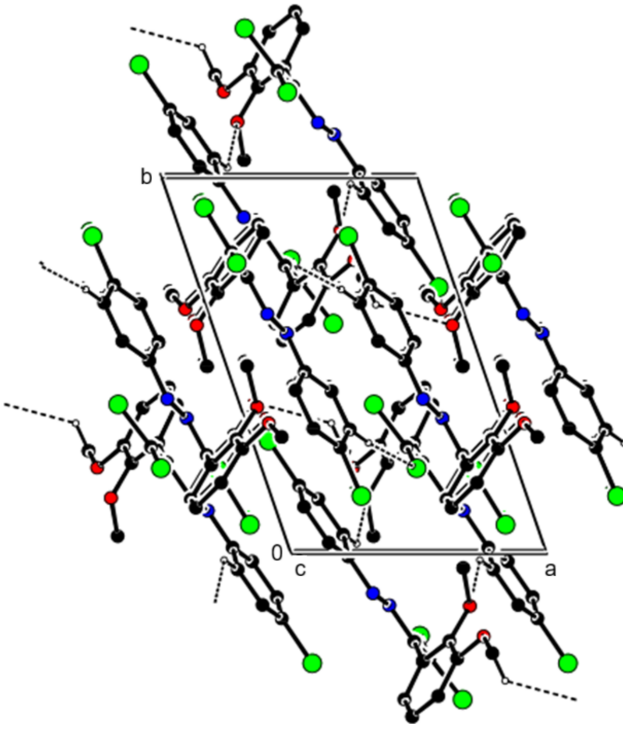


Figure 8
View of the C—H···O and C—H—Cl interactions (**II**) along the *c* axis. H atoms not involved in hydrogen bonding were removed for clarity.

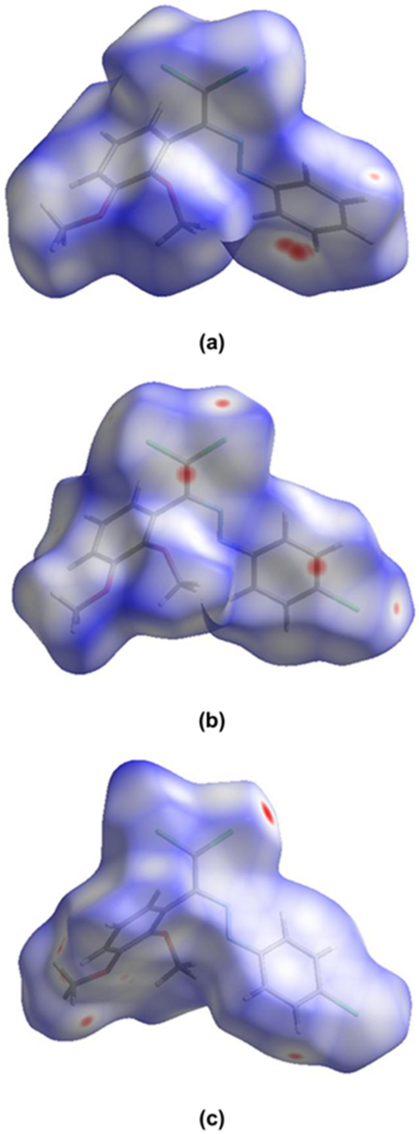


Figure 9
The Hirshfeld surfaces of (*a*) (**I**), (*b*) (**II**) molecule *A* and (*c*) (**II**) molecule *B* plotted over $d_{\rm norm}$.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 6.00, update of April 2025; Groom *et al.*, 2016) for the (*E*)-1-(2,2-dichloro-1-phenylethen-1-yl)-2-phenyldiazene moiety resulted in 39 hits. Eight compounds are most similar to the title compound, *viz*. those with CSD refcodes POCXIS

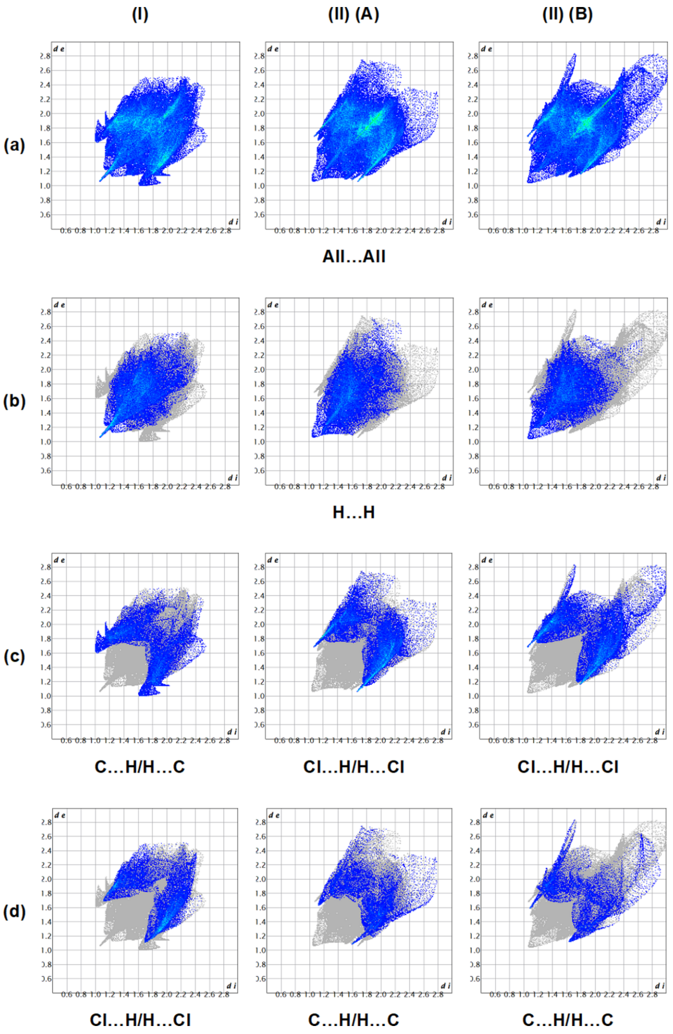


Figure 10
The full two-dimensional fingerprint plots for (**I**) and (**II**), showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) C···H/H···C for (**I**) [Cl···H/H···Cl for molecules *A* and *B* of (**II**)] and (*d*) Cl···H/H···Cl for (**I**) (C···H/H···C for molecules *A* and *B* of (**II**)] interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

(Shikhaliyev *et al.*, 2024), NIKXEO (Maharramov *et al.*, 2023), TAZDIL (Atioğlu *et al.*, 2022), HEHKEO (Akkurt *et al.*, 2022), PAXDOL (Çelikesir *et al.*, 2022), CANVUM (Shikhaliyev *et al.*, 2021), GUPHIL (Özkaraca *et al.*, 2020), HODQAV (Shikhaliyev *et al.*, 2019).

In the crystal of POCXIS, molecules are linked by C—H···N hydrogen bonds, forming chains with *C*(6) motifs parallel to the *b* axis. Short intermolecular Cl···O contacts of 2.8421 (16) Å and weak van der Waals interactions between these chains consolidate the crystal structure. In the crystal structure of NIKXEO, molecules are linked by C—H···π and C—Cl···π interactions, forming layers parallel to $(\bar{1}01)$. The cohesion of the packing is ensured by van der Waals forces between these layers. The molecules in TAZDIL are joined into layers parallel to (011) by C—H···O and C—H···F hydrogen bonds. C—Br···π and C—F···π contacts, as well as π–π stacking interactions consolidate the crystal packing. C—H···Br interactions connect the molecules in the crystal of the polymorph-1 of HEHKEO, resulting in zigzag *C*(8) chains parallel to [100]. These chains are connected by C—Br···π interactions into layers parallel to (001). van der Waals interactions between the layers contribute to the crystal cohesion. The molecules in the crystal of PAXDOL are connected into chains running parallel to [001] by C—H···O hydrogen bonds. C—F···π contacts and π–π stacking interactions help to consolidate the crystal packing, and short Br···O [2.9828 (13) Å] distances are also observed. In CANVUM, the molecules are linked by C—H···N interactions along [100], forming a *C*(6) chain. The molecules are further connected by C—Cl···π interactions and face-to-face π–π stacking interactions, resulting in ribbons along [100]. In GUPHIL, molecules are associated into inversion dimers *via* short Cl···Cl contacts [3.3763 (9) Å]. In HODQAV, molecules are stacked in columns along [100] *via* weak C—H···Cl hydrogen bonds and face-to-face π–π stacking interactions. The crystal packing is further consolidated by short Cl···Cl contacts.

5. Synthesis and crystallization

Compounds (**I**) and (**II**) were synthesized according to a literature protocol (Shikhaliyev *et al.*, 2018). For (**I**), a 20 ml screw-neck vial was charged with dimethylsulfoxide (DMSO) (10 ml), (*E*)-1-(4-chlorophenyl)-2-(2,3-dimethoxybenzylidene)hydrazine (290 mg, 1 mmol), tetramethylethylenediamine (TMEDA) (295 mg, 2.5 mmol), CuCl (2 mg, 0.02 mmol) and CCl_4 (1 mmol). After 2–3 h (until TLC analysis showed complete consumption of the corresponding Schiff base), the reaction mixture was poured into a 0.01 *M* solution of HCl (100 ml, pH = 2–3), and extracted with dichloromethane (3 × 20 ml). The combined organic phase was washed with water (3 × 50 ml), brine (30 ml), dried over anhydrous Na_2SO_4 and concentrated in vacuum using a rotary evaporator. The residue was purified by column chromatography on silica gel using appropriate mixtures of hexane and dichloromethane (*v*/*v*: 5/1–3/1–1/1). A red solid was obtained (yield 65%); m.p. 365 K. ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.71–7.69 (*m*, 2H, arom), 7.49–7.45 (*m*, 2H, arom), 7.30–7.25 (*m*, 1H, arom), 7.19–7.11 (*m*, 3H, arom), 3.71 (*s*, 3H, $-OCH_3$), 3.84 (*s*, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) 152.4, 151.7, 149.5, 133.8, 130.7, 129.2, 128.3, 128.1, 127.7, 124.9, 121.7, 117.6, 60.6, 56.0.

For (**II**), the procedure was the same as that for (**I**) using methyl (*E*)-1-(4-chlorophenyl)-2-(2,3-dimethoxybenzylidene) hydrazine (290 mg, 1 mmol). A red solid was obtained (yield 78%); m.p. 399 K. ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.67–7.60 (*m*, 1H, arom), 7.52–7.45 (*m*, 1H, arom), 7.18–7.05 (*m*, 1H, arom), 3.75 (*s*, 1H, $-OCH_3$), 3.98 (*s*, 1H, $-OCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) 151.8, 151.0, 149.7, 136.7, 133.3, 129.1, 128.4, 128.0, 127.6, 124.6, 117.7, 114.6, 67.6, 54.6.

In each case, the obtained compound was dissolved in dichloromethane and then left at room temperature for slow evaporation; red single crystals suitable for X-ray diffraction analysis started to form after *ca* 2 d.

Table 3
Experimental details.

	(**I**)	(**II**)
Crystal data		
Chemical formula	$C_{16}H_{14}Cl_2N_2O_2$	$C_{16}H_{13}Cl_3N_2O_2$
M_r	337.19	371.63
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$
Temperature (K)	100	100
a, b, c (Å)	7.30389 (4), 30.68147 (13), 7.42658 (4)	8.2181 (11), 13.3651 (17), 16.687 (2)
α, β, γ (°)	90, 109.7560 (6), 90	108.139 (3), 94.732 (3), 106.396 (3)
V (Å^3)	1566.30 (2)	1641.5 (4)
Z	4	4
Radiation type	Cu $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	3.80	0.57
Crystal size (mm)	0.13 × 0.11 × 0.06	0.30 × 0.20 × 0.20
Data collection		
Diffractometer	Rigaku XtaLAB Synergy-S, HyPix-6000HE area-detector	Bruker D8 QUEST PHOTON-III area detector
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2025)	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.641, 0.796	0.656, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	81705, 3424, 3376	39419, 11888, 10714
R_{int}	0.046	0.023
($\sin \theta/\lambda)_{max}$ (Å^{-1})	0.639	0.758
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.082, 1.06	0.027, 0.074, 1.05
No. of reflections	3424	11888
No. of parameters	201	419
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.33, −0.36	0.48, −0.36

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *APEX3* and *SAINT* (Bruker, 2018), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were positioned geometrically and refined using a riding model [C—H = 0.95–0.98 Å and U_{iso}(H) = 1.2 or 1.5 U_{eq}(C)].

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The contributions of the authors are as follows: conceptualization NQS, MA and GTA; synthesis NAM, PAH, GVB; X-ray analysis MA, GAM; writing (review and editing of the manuscript) MA, NQS and GTA; funding acquisition AB, NQS and PAH; supervision NQS and MA.

References

Akkurt, M., Yıldırım, S. Ö., Shikhaliyev, N. Q., Mammadova, N. A., Niyazova, A. A., Khrustalev, V. N. & Bhattarai, A. (2022). *Acta Cryst.* E**78**, 732–736.

Al-Mudhaffer, M. F., Al-Ahmad, A. Y., Hassan, Q. M. A. & Emshary, C. A. (2016). *Optik* **127**, 1160-1166.

Atioğlu, Z., Akkurt, M., Shikhaliyev, N. Q., Mammadova, N. A., Babayeva, G. V., Khrustalev, V. N. & Bhattarai, A. (2022). *Acta Cryst.* E**78**, 530–535.

Bruker (2018). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Çelikesir, S. T., Akkurt, M., Shikhaliyev, N. Q., Mammadova, N. A., Suleymanova, G. T., Khrustalev, V. N. & Bhattarai, A. (2022). *Acta Cryst.* E**78**, 404–408.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Garg, S. K. & Tripathi, M. (2017). *Res. J. Microbiol.* **12**, 1–19.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Khan, M. N., Parmar, D. K. & Das, D. (2021). *Mini Rev. Med. Chem.* **21**, 1071–1084.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Maharramov, A., Shikhaliyev, N. Q., Qajar, A., Atakishiyeva, G. T., Niyazova, A., Khrustalev, V. N., Akkurt, M., Yıldırım, S. Ö. & Bhattarai, A. (2023). *Acta Cryst.* E**79**, 637–643.

Mohr, G. J. & Wolfbeis, O. S. (1994). *Anal. Chim. Acta* **292**, 41–48.

O'Neill, C., Lopez, A., Esteves, S., Hawkes, F. R., Hawkes, D. L. & Wilcox, S. (2000). *Appl. Microbiol. Biotechnol.* **53**, 249–254.

Özkaraca, K., Akkurt, M., Shikhaliyev, N. Q., Askerova, U. F., Suleymanova, G. T., Mammadova, G. Z. & Shadrack, D. M. (2020). *Acta Cryst.* E**76**, 1251–1254.

Rigaku OD (2021). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.

Rigaku OD (2025). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Shikhaliyev, N. Q., Ahmadova, N. E., Gurbanov, A. V., Maharramov, A. M., Mammadova, G. Z., Nenajdenko, V. G., Zubkov, F. I., Mahmudov, K. T. & Pombeiro, A. J. L. (2018). *Dyes Pigments* **150**, 377–381.

Shikhaliyev, N. Q., Çelikesir, S. T., Akkurt, M., Bagirova, K. N., Suleymanova, G. T. & Toze, F. A. A. (2019). *Acta Cryst.* E**75**, 465–469.

Shikhaliyev, N. Q., İbrahimova, S. A., Atakishiyeva, G. T., Ahmedova, N. E., Babayeva, G. V., Khrustalev, V. N., Atioğlu, Z., Akkurt, M. & Bhattarai, A. (2024). *Acta Cryst.* E**80**, 184–190.

Shikhaliyev, N. Q., Özkaraca, K., Akkurt, M., Bagirova, X. N., Suleymanova, G. T., Abdulov, M. S. & Mlowe, S. (2021). *Acta Cryst.* E**77**, 1158–1163.

Singh, P. K. & Singh, R. L. (2017). *Int. J. Appl. Sci. Biotechnol.* **5**, 108–126.

Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.

Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.

supporting information

Acta Cryst. (2026). E**82**, 156-162 [https://doi.org/10.1107/S2056989026000137]

Syntheses, crystal structures and Hirshfeld surface analyses of (*E*)-1-[2,2-dichloro-1-(2,3-dimethoxyphenyl)ethen-1-yl]-2-phenyldiazene and (*E*)-1-(4-chlorophenyl)-2-[2,2-dichloro-1-(2,3-dimethoxyphenyl)ethen-1-yl]diazene

Namiq Q. Shikhaliyev, Naila Mammadova, Gulnar T. Atakishiyeva, Peri A. Huseynova, Gulnara V. Babayeva, Gulnaz A. Mirzayeva, Mehmet Akkurt and Ajaya Bhattarai

Computing details

(*E*)-1-[2,2-Dichloro-1-(2,3-dimethoxyphenyl)ethen-1-yl]-2-phenyldiazene (I)

Crystal data

$C_{16}H_{14}Cl_2N_2O_2$
$M_r = 337.19$
Monoclinic, $P2_1/c$
$a = 7.30389$ (4) Å
$b = 30.68147$ (13) Å
$c = 7.42658$ (4) Å
$\beta = 109.7560$ (6)°
$V = 1566.30$ (2) Å^3
$Z = 4$

$F(000) = 696$
$D_x = 1.430$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 60750 reflections
$\theta = 2.9$–79.6°
$\mu = 3.80$ mm^{-1}
$T = 100$ K
Prism, brown
0.13 × 0.11 × 0.06 mm

Data collection

Rigaku XtaLAB Synergy-S, HyPix-6000HE area-detector diffractometer
Radiation source: micro-focus sealed X-ray tube
φ and ω scans
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2025)
$T_{min} = 0.641$, $T_{max} = 0.796$

81705 measured reflections
3424 independent reflections
3376 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 80.0°$, $\theta_{min} = 2.9°$
$h = -9 \rightarrow 9$
$k = -39 \rightarrow 39$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.082$
$S = 1.06$
3424 reflections
201 parameters
0 restraints
Primary atom site location: difference Fourier map

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 1.1051P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
Cl1	0.29682 (5)	0.65828 (2)	0.93930 (5)	0.02571 (10)
Cl2	0.52050 (5)	0.72971 (2)	0.87184 (5)	0.02478 (10)
O1	0.73197 (15)	0.57980 (3)	0.88689 (15)	0.0228 (2)
O2	0.60438 (16)	0.49625 (3)	0.82871 (15)	0.0249 (2)
N1	0.63222 (17)	0.66977 (4)	0.62019 (17)	0.0194 (2)
N2	0.66515 (17)	0.64600 (4)	0.49630 (17)	0.0193 (2)
C1	0.5041 (2)	0.65062 (4)	0.7039 (2)	0.0186 (3)
C2	0.4487 (2)	0.67660 (5)	0.8224 (2)	0.0205 (3)
C3	0.4334 (2)	0.60489 (4)	0.6629 (2)	0.0183 (3)
C4	0.5525 (2)	0.57056 (4)	0.75418 (19)	0.0185 (3)
C5	0.4827 (2)	0.52744 (5)	0.7230 (2)	0.0201 (3)
C6	0.2983 (2)	0.51953 (5)	0.5918 (2)	0.0232 (3)
H6	0.251670	0.490476	0.566572	0.028*
C7	0.1820 (2)	0.55417 (5)	0.4975 (2)	0.0255 (3)
H7	0.056650	0.548542	0.407235	0.031*
C8	0.2470 (2)	0.59666 (5)	0.5339 (2)	0.0233 (3)
H8	0.165342	0.620149	0.471536	0.028*
C9	0.8957 (2)	0.56394 (6)	0.8398 (3)	0.0316 (4)
H9A	0.895488	0.577293	0.719845	0.047*
H9B	0.886635	0.532197	0.824871	0.047*
H9C	1.016507	0.571543	0.942622	0.047*
C10	0.5289 (3)	0.45272 (5)	0.8119 (2)	0.0284 (3)
H10A	0.502301	0.442238	0.680886	0.043*
H10B	0.408232	0.452573	0.842048	0.043*
H10C	0.624663	0.433599	0.901379	0.043*
C11	0.7989 (2)	0.66527 (4)	0.4167 (2)	0.0184 (3)
C12	0.7998 (2)	0.64778 (5)	0.2436 (2)	0.0202 (3)
H12	0.713531	0.624722	0.184687	0.024*
C13	0.9273 (2)	0.66424 (5)	0.1579 (2)	0.0222 (3)
H13	0.925250	0.653168	0.037768	0.027*
C14	1.0577 (2)	0.69685 (5)	0.2478 (2)	0.0226 (3)
H14	1.146914	0.707599	0.190471	0.027*
C15	1.0584 (2)	0.71388 (5)	0.4217 (2)	0.0230 (3)
H15	1.148738	0.736065	0.482808	0.028*
C16	0.9280 (2)	0.69868 (4)	0.5064 (2)	0.0206 (3)
H16	0.926334	0.710772	0.623627	0.025*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02833 (18)	0.02687 (18)	0.02930 (19)	−0.00008 (13)	0.01938 (15)	−0.00127 (13)
Cl2	0.03005 (19)	0.01812 (17)	0.02945 (19)	−0.00041 (12)	0.01436 (15)	−0.00447 (12)
O1	0.0207 (5)	0.0220 (5)	0.0233 (5)	−0.0005 (4)	0.0046 (4)	−0.0033 (4)
O2	0.0309 (5)	0.0166 (5)	0.0272 (5)	−0.0004 (4)	0.0098 (4)	0.0016 (4)
N1	0.0206 (5)	0.0185 (5)	0.0218 (6)	0.0010 (4)	0.0105 (5)	0.0007 (4)
N2	0.0191 (5)	0.0197 (5)	0.0206 (6)	−0.0003 (4)	0.0088 (5)	−0.0007 (4)
C1	0.0184 (6)	0.0182 (6)	0.0203 (7)	0.0006 (5)	0.0079 (5)	0.0007 (5)
C2	0.0211 (6)	0.0202 (6)	0.0225 (7)	0.0005 (5)	0.0103 (5)	0.0006 (5)
C3	0.0199 (6)	0.0191 (6)	0.0195 (6)	−0.0015 (5)	0.0114 (5)	−0.0014 (5)
C4	0.0201 (6)	0.0203 (6)	0.0175 (6)	−0.0019 (5)	0.0095 (5)	−0.0029 (5)
C5	0.0248 (7)	0.0186 (6)	0.0208 (7)	−0.0003 (5)	0.0128 (6)	−0.0005 (5)
C6	0.0253 (7)	0.0211 (7)	0.0271 (7)	−0.0065 (5)	0.0138 (6)	−0.0044 (6)
C7	0.0194 (7)	0.0290 (8)	0.0280 (7)	−0.0046 (6)	0.0079 (6)	−0.0040 (6)
C8	0.0192 (6)	0.0240 (7)	0.0278 (7)	0.0014 (5)	0.0093 (6)	0.0005 (6)
C9	0.0206 (7)	0.0295 (8)	0.0432 (10)	0.0007 (6)	0.0090 (7)	−0.0034 (7)
C10	0.0393 (9)	0.0158 (7)	0.0332 (8)	−0.0017 (6)	0.0163 (7)	0.0016 (6)
C11	0.0194 (6)	0.0172 (6)	0.0204 (6)	0.0017 (5)	0.0091 (5)	0.0018 (5)
C12	0.0208 (6)	0.0208 (6)	0.0185 (6)	−0.0012 (5)	0.0061 (5)	−0.0015 (5)
C13	0.0251 (7)	0.0252 (7)	0.0178 (7)	0.0006 (6)	0.0093 (6)	0.0000 (5)
C14	0.0248 (7)	0.0217 (7)	0.0258 (7)	0.0000 (5)	0.0144 (6)	0.0035 (6)
C15	0.0258 (7)	0.0181 (6)	0.0277 (7)	−0.0033 (5)	0.0124 (6)	−0.0018 (6)
C16	0.0239 (7)	0.0188 (6)	0.0214 (7)	−0.0008 (5)	0.0107 (6)	−0.0029 (5)

Geometric parameters (Å, º)

Cl1—C2	1.7182 (14)	C8—H8	0.9500
Cl2—C2	1.7131 (15)	C9—H9A	0.9800
O1—C4	1.3772 (17)	C9—H9B	0.9800
O1—C9	1.4395 (19)	C9—H9C	0.9800
O2—C5	1.3604 (18)	C10—H10A	0.9800
O2—C10	1.4341 (17)	C10—H10B	0.9800
N1—N2	1.2593 (17)	C10—H10C	0.9800
N1—C1	1.4141 (18)	C11—C12	1.3950 (19)
N2—C11	1.4296 (18)	C11—C16	1.3993 (19)
C1—C2	1.347 (2)	C12—C13	1.389 (2)
C1—C3	1.4905 (19)	C12—H12	0.9500
C3—C4	1.388 (2)	C13—C14	1.387 (2)
C3—C8	1.398 (2)	C13—H13	0.9500
C4—C5	1.4086 (19)	C14—C15	1.391 (2)
C5—C6	1.391 (2)	C14—H14	0.9500
C6—C7	1.393 (2)	C15—C16	1.388 (2)
C6—H6	0.9500	C15—H15	0.9500
C7—C8	1.382 (2)	C16—H16	0.9500
C7—H7	0.9500		

C4—O1—C9	115.13 (11)	O1—C9—H9B	109.5
C5—O2—C10	116.62 (12)	H9A—C9—H9B	109.5
N2—N1—C1	113.49 (12)	O1—C9—H9C	109.5
N1—N2—C11	112.86 (11)	H9A—C9—H9C	109.5
C2—C1—N1	115.51 (12)	H9B—C9—H9C	109.5
C2—C1—C3	122.04 (13)	O2—C10—H10A	109.5
N1—C1—C3	122.44 (12)	O2—C10—H10B	109.5
C1—C2—Cl2	124.42 (11)	H10A—C10—H10B	109.5
C1—C2—Cl1	121.64 (11)	O2—C10—H10C	109.5
Cl2—C2—Cl1	113.94 (8)	H10A—C10—H10C	109.5
C4—C3—C8	120.14 (13)	H10B—C10—H10C	109.5
C4—C3—C1	119.85 (12)	C12—C11—C16	120.56 (13)
C8—C3—C1	120.01 (13)	C12—C11—N2	115.99 (12)
O1—C4—C3	118.77 (12)	C16—C11—N2	123.41 (12)
O1—C4—C5	120.99 (13)	C13—C12—C11	119.68 (13)
C3—C4—C5	120.01 (13)	C13—C12—H12	120.2
O2—C5—C6	124.78 (13)	C11—C12—H12	120.2
O2—C5—C4	115.87 (13)	C14—C13—C12	119.95 (13)
C6—C5—C4	119.34 (13)	C14—C13—H13	120.0
C5—C6—C7	120.04 (13)	C12—C13—H13	120.0
C5—C6—H6	120.0	C13—C14—C15	120.28 (13)
C7—C6—H6	120.0	C13—C14—H14	119.9
C8—C7—C6	120.71 (14)	C15—C14—H14	119.9
C8—C7—H7	119.6	C16—C15—C14	120.46 (13)
C6—C7—H7	119.6	C16—C15—H15	119.8
C7—C8—C3	119.66 (14)	C14—C15—H15	119.8
C7—C8—H8	120.2	C15—C16—C11	119.04 (13)
C3—C8—H8	120.2	C15—C16—H16	120.5
O1—C9—H9A	109.5	C11—C16—H16	120.5

C1—N1—N2—C11	−178.40 (11)	C3—C4—C5—O2	−175.49 (12)
N2—N1—C1—C2	−173.35 (13)	O1—C4—C5—C6	178.10 (12)
N2—N1—C1—C3	6.15 (19)	C3—C4—C5—C6	3.7 (2)
N1—C1—C2—Cl2	0.89 (19)	O2—C5—C6—C7	176.99 (13)
C3—C1—C2—Cl2	−178.62 (11)	C4—C5—C6—C7	−2.1 (2)
N1—C1—C2—Cl1	−178.88 (10)	C5—C6—C7—C8	−0.6 (2)
C3—C1—C2—Cl1	1.6 (2)	C6—C7—C8—C3	1.7 (2)
C2—C1—C3—C4	−101.19 (16)	C4—C3—C8—C7	−0.1 (2)
N1—C1—C3—C4	79.34 (17)	C1—C3—C8—C7	−179.60 (13)
C2—C1—C3—C8	78.30 (18)	N1—N2—C11—C12	−161.90 (12)
N1—C1—C3—C8	−101.17 (16)	N1—N2—C11—C16	20.25 (19)
C9—O1—C4—C3	−117.64 (14)	C16—C11—C12—C13	−1.2 (2)
C9—O1—C4—C5	67.90 (17)	N2—C11—C12—C13	−179.13 (13)
C8—C3—C4—O1	−177.11 (12)	C11—C12—C13—C14	2.3 (2)
C1—C3—C4—O1	2.38 (19)	C12—C13—C14—C15	−1.5 (2)
C8—C3—C4—C5	−2.6 (2)	C13—C14—C15—C16	−0.4 (2)
C1—C3—C4—C5	176.89 (12)	C14—C15—C16—C11	1.5 (2)
C10—O2—C5—C6	−4.7 (2)	C12—C11—C16—C15	−0.7 (2)

C10—O2—C5—C4	174.42 (12)	N2—C11—C16—C15	177.09 (13)
O1—C4—C5—O2	−1.09 (19)		

Hydrogen-bond geometry (Å, º)

Cg and *Cg*2 are the centroids of the C3–C8 and C11–C16 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*B*···O2	0.98	2.35	2.955 (2)	119
C8—H8···*Cg*2^{i}	0.95	2.52	3.4665 (16)	174
C10—H10*A*···*Cg*1^{ii}	0.98	2.77	3.6231 (18)	146

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

(*E*)-1-(4-Chlorophenyl)-2-[2,2-dichloro-1-(2,3-dimethoxyphenyl)ethen-1-yl]diazene (II)

Crystal data

$C_{16}H_{13}Cl_3N_2O_2$
M_r = 371.63
Triclinic, $P\bar{1}$
a = 8.2181 (11) Å
b = 13.3651 (17) Å
c = 16.687 (2) Å
α = 108.139 (3)°
β = 94.732 (3)°
γ = 106.396 (3)°
V = 1641.5 (4) Å^3
Z = 4
$F(000)$ = 760
D_x = 1.504 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9797 reflections
θ = 2.5–32.6°
μ = 0.57 mm^{-1}
T = 100 K
Prism, red
0.30 × 0.20 × 0.20 mm

Data collection

Bruker D8 QUEST PHOTON-III area detector diffractometer
Radiation source: fine-focus sealed X-ray tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.656, T_{max} = 0.746
39419 measured reflections
11888 independent reflections
10714 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 32.6°, θ_{min} = 2.5°
$h = -12 \rightarrow 12$
$k = -20 \rightarrow 20$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.074
S = 1.05
11888 reflections
419 parameters
0 restraints
Primary atom site location: difference Fourier map
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 0.5553P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Special details

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

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
Cl1	0.52462 (3)	0.39382 (2)	0.61838 (2)	0.01884 (4)
Cl2	0.60551 (3)	0.22480 (2)	0.67158 (2)	0.01681 (4)
Cl3	0.93613 (3)	−0.29765 (2)	0.35426 (2)	0.02135 (5)
O1	0.37126 (8)	0.14223 (5)	0.37547 (4)	0.01618 (11)
O2	0.35903 (9)	0.22142 (7)	0.24322 (4)	0.02241 (14)
N1	0.68510 (9)	0.14189 (6)	0.50182 (5)	0.01367 (12)
N2	0.73277 (9)	0.10900 (6)	0.43084 (5)	0.01397 (12)
C1	0.63666 (10)	0.23844 (7)	0.51515 (5)	0.01289 (13)
C2	0.59557 (10)	0.28070 (7)	0.59243 (5)	0.01407 (13)
C3	0.62956 (11)	0.28996 (7)	0.44848 (5)	0.01406 (13)
C4	0.49846 (11)	0.23529 (7)	0.37639 (5)	0.01431 (14)
C5	0.49164 (12)	0.28101 (8)	0.31110 (6)	0.01749 (15)
C6	0.61659 (13)	0.38110 (8)	0.31980 (7)	0.02166 (17)
H6	0.613973	0.411847	0.275667	0.026*
C7	0.74526 (13)	0.43615 (8)	0.39303 (7)	0.02283 (18)
H7	0.828671	0.504994	0.398958	0.027*
C8	0.75279 (12)	0.39143 (7)	0.45739 (6)	0.01894 (16)
H8	0.840912	0.429363	0.507151	0.023*
C9	0.34619 (13)	0.03990 (8)	0.30589 (6)	0.02063 (16)
H9A	0.266099	−0.022038	0.316964	0.031*
H9B	0.457253	0.027063	0.301213	0.031*
H9C	0.298159	0.045034	0.252128	0.031*
C10	0.34774 (15)	0.26519 (11)	0.17551 (7)	0.0288 (2)
H10A	0.247916	0.215008	0.130545	0.043*
H10B	0.453296	0.271712	0.151302	0.043*
H10C	0.334288	0.338809	0.198379	0.043*
C11	0.78013 (10)	0.01095 (7)	0.41738 (5)	0.01290 (13)
C12	0.77031 (10)	−0.04677 (7)	0.47494 (5)	0.01369 (13)
H12	0.730021	−0.021214	0.526810	0.016*
C13	0.81964 (11)	−0.14140 (7)	0.45591 (6)	0.01522 (14)
H13	0.814229	−0.180789	0.494720	0.018*
C14	0.87724 (11)	−0.17801 (7)	0.37917 (6)	0.01531 (14)
C15	0.88686 (11)	−0.12229 (7)	0.32107 (6)	0.01720 (15)
H15	0.925946	−0.148619	0.268961	0.021*
C16	0.83798 (12)	−0.02699 (7)	0.34081 (6)	0.01643 (14)
H16	0.844063	0.012369	0.301954	0.020*
Cl4	0.87637 (4)	0.07775 (2)	−0.06471 (2)	0.02627 (5)
Cl5	0.82442 (3)	0.22427 (2)	−0.15224 (2)	0.02417 (5)
Cl6	0.64871 (3)	0.84635 (2)	0.08704 (2)	0.02619 (5)
O3	1.06237 (8)	0.39299 (5)	0.15401 (4)	0.01643 (11)
O4	1.08535 (9)	0.35191 (6)	0.30450 (4)	0.02088 (13)
N3	0.77232 (10)	0.36141 (6)	0.00963 (5)	0.01578 (13)
N4	0.72217 (10)	0.41370 (6)	0.07466 (5)	0.01555 (13)
C17	0.80095 (11)	0.26384 (7)	0.01445 (5)	0.01528 (14)
C18	0.82960 (12)	0.19689 (8)	−0.05837 (6)	0.01803 (15)

C19	0.80494 (11)	0.23840 (7)	0.09495 (5)	0.01545 (14)
C20	0.93752 (11)	0.30709 (7)	0.16454 (5)	0.01428 (14)
C21	0.94769 (12)	0.28288 (7)	0.24077 (5)	0.01667 (15)
C22	0.81979 (13)	0.19287 (8)	0.24688 (6)	0.02044 (17)
H22	0.823347	0.177453	0.298738	0.025*
C23	0.68692 (13)	0.12549 (8)	0.17728 (7)	0.02210 (17)
H23	0.600506	0.064214	0.182018	0.027*
C24	0.67918 (12)	0.14677 (8)	0.10112 (6)	0.01977 (16)
H24	0.589309	0.099575	0.053525	0.024*
C25	1.07785 (14)	0.50288 (8)	0.21075 (6)	0.02244 (17)
H25A	1.155871	0.558731	0.192716	0.034*
H25B	1.124324	0.512107	0.269563	0.034*
H25C	0.963877	0.512497	0.208544	0.034*
C26	1.11744 (14)	0.31627 (10)	0.37516 (6)	0.02507 (19)
H26A	1.226263	0.367450	0.413125	0.038*
H26B	1.125226	0.241010	0.353401	0.038*
H26C	1.022764	0.315986	0.407247	0.038*
C27	0.70345 (11)	0.51546 (7)	0.07168 (5)	0.01464 (14)
C28	0.76452 (12)	0.56438 (7)	0.01249 (6)	0.01693 (15)
H28	0.818802	0.528373	−0.030412	0.020*
C29	0.74563 (12)	0.66564 (8)	0.01657 (6)	0.01828 (15)
H29	0.786462	0.699392	−0.023503	0.022*
C30	0.66612 (12)	0.71729 (7)	0.08007 (6)	0.01769 (15)
C31	0.60443 (13)	0.66986 (8)	0.13918 (6)	0.02090 (17)
H31	0.549572	0.705915	0.181751	0.025*
C32	0.62434 (12)	0.56855 (8)	0.13499 (6)	0.01901 (16)
H32	0.583913	0.535295	0.175387	0.023*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02007 (9)	0.01638 (9)	0.02093 (9)	0.00975 (7)	0.00648 (7)	0.00359 (7)
Cl2	0.01901 (9)	0.02017 (9)	0.01194 (8)	0.00688 (7)	0.00406 (6)	0.00578 (7)
Cl3	0.02032 (9)	0.01497 (9)	0.03167 (11)	0.00974 (7)	0.00761 (8)	0.00779 (8)
O1	0.0172 (3)	0.0169 (3)	0.0139 (3)	0.0034 (2)	0.0043 (2)	0.0062 (2)
O2	0.0260 (3)	0.0327 (4)	0.0171 (3)	0.0146 (3)	0.0051 (2)	0.0154 (3)
N1	0.0155 (3)	0.0132 (3)	0.0131 (3)	0.0058 (2)	0.0034 (2)	0.0045 (2)
N2	0.0166 (3)	0.0132 (3)	0.0140 (3)	0.0064 (2)	0.0046 (2)	0.0055 (2)
C1	0.0138 (3)	0.0122 (3)	0.0130 (3)	0.0046 (3)	0.0029 (2)	0.0044 (3)
C2	0.0141 (3)	0.0136 (3)	0.0146 (3)	0.0056 (3)	0.0032 (3)	0.0038 (3)
C3	0.0164 (3)	0.0136 (3)	0.0158 (3)	0.0074 (3)	0.0060 (3)	0.0070 (3)
C4	0.0164 (3)	0.0155 (3)	0.0153 (3)	0.0077 (3)	0.0063 (3)	0.0081 (3)
C5	0.0209 (4)	0.0230 (4)	0.0178 (4)	0.0137 (3)	0.0087 (3)	0.0124 (3)
C6	0.0275 (4)	0.0234 (4)	0.0274 (4)	0.0155 (4)	0.0144 (4)	0.0181 (4)
C7	0.0256 (4)	0.0167 (4)	0.0328 (5)	0.0083 (3)	0.0123 (4)	0.0147 (4)
C8	0.0196 (4)	0.0144 (4)	0.0240 (4)	0.0053 (3)	0.0066 (3)	0.0078 (3)
C9	0.0261 (4)	0.0180 (4)	0.0150 (4)	0.0042 (3)	0.0031 (3)	0.0049 (3)
C10	0.0344 (5)	0.0474 (6)	0.0228 (4)	0.0253 (5)	0.0113 (4)	0.0245 (5)

C11	0.0150 (3)	0.0122 (3)	0.0131 (3)	0.0056 (3)	0.0041 (2)	0.0052 (3)
C12	0.0151 (3)	0.0139 (3)	0.0134 (3)	0.0051 (3)	0.0038 (3)	0.0059 (3)
C13	0.0151 (3)	0.0143 (3)	0.0177 (4)	0.0050 (3)	0.0029 (3)	0.0074 (3)
C14	0.0143 (3)	0.0119 (3)	0.0207 (4)	0.0056 (3)	0.0042 (3)	0.0056 (3)
C15	0.0199 (4)	0.0161 (4)	0.0176 (4)	0.0079 (3)	0.0078 (3)	0.0057 (3)
C16	0.0218 (4)	0.0159 (4)	0.0150 (3)	0.0083 (3)	0.0076 (3)	0.0070 (3)
Cl4	0.04214 (14)	0.02113 (10)	0.01987 (10)	0.01977 (10)	0.00606 (9)	0.00440 (8)
Cl5	0.03724 (12)	0.02648 (11)	0.01195 (9)	0.01681 (9)	0.00405 (8)	0.00530 (8)
Cl6	0.02955 (11)	0.01739 (10)	0.03471 (13)	0.01311 (9)	0.00505 (9)	0.00860 (9)
O3	0.0186 (3)	0.0153 (3)	0.0166 (3)	0.0047 (2)	0.0048 (2)	0.0075 (2)
O4	0.0265 (3)	0.0255 (3)	0.0147 (3)	0.0114 (3)	0.0034 (2)	0.0101 (2)
N3	0.0188 (3)	0.0153 (3)	0.0143 (3)	0.0077 (3)	0.0029 (2)	0.0049 (2)
N4	0.0173 (3)	0.0153 (3)	0.0157 (3)	0.0072 (2)	0.0038 (2)	0.0056 (2)
C17	0.0176 (3)	0.0142 (3)	0.0144 (3)	0.0065 (3)	0.0025 (3)	0.0045 (3)
C18	0.0236 (4)	0.0175 (4)	0.0139 (3)	0.0100 (3)	0.0023 (3)	0.0040 (3)
C19	0.0197 (4)	0.0142 (3)	0.0152 (3)	0.0080 (3)	0.0057 (3)	0.0061 (3)
C20	0.0181 (3)	0.0139 (3)	0.0145 (3)	0.0079 (3)	0.0058 (3)	0.0068 (3)
C21	0.0231 (4)	0.0182 (4)	0.0148 (3)	0.0119 (3)	0.0073 (3)	0.0083 (3)
C22	0.0304 (4)	0.0193 (4)	0.0213 (4)	0.0140 (3)	0.0140 (3)	0.0126 (3)
C23	0.0288 (4)	0.0151 (4)	0.0275 (4)	0.0087 (3)	0.0143 (4)	0.0106 (3)
C24	0.0226 (4)	0.0139 (4)	0.0225 (4)	0.0055 (3)	0.0069 (3)	0.0056 (3)
C25	0.0292 (5)	0.0150 (4)	0.0197 (4)	0.0048 (3)	−0.0016 (3)	0.0051 (3)
C26	0.0324 (5)	0.0386 (6)	0.0165 (4)	0.0223 (4)	0.0088 (3)	0.0153 (4)
C27	0.0163 (3)	0.0149 (3)	0.0133 (3)	0.0064 (3)	0.0026 (3)	0.0046 (3)
C28	0.0215 (4)	0.0174 (4)	0.0153 (3)	0.0095 (3)	0.0062 (3)	0.0067 (3)
C29	0.0226 (4)	0.0176 (4)	0.0177 (4)	0.0089 (3)	0.0047 (3)	0.0079 (3)
C30	0.0187 (4)	0.0143 (3)	0.0201 (4)	0.0077 (3)	0.0013 (3)	0.0044 (3)
C31	0.0247 (4)	0.0196 (4)	0.0210 (4)	0.0116 (3)	0.0088 (3)	0.0055 (3)
C32	0.0240 (4)	0.0192 (4)	0.0172 (4)	0.0101 (3)	0.0087 (3)	0.0069 (3)

Geometric parameters (Å, º)

Cl1—C2	1.7161 (9)	Cl4—C18	1.7151 (9)
Cl2—C2	1.7149 (9)	Cl5—C18	1.7159 (9)
Cl3—C14	1.7379 (9)	Cl6—C30	1.7397 (9)
O1—C4	1.3753 (10)	O3—C20	1.3755 (10)
O1—C9	1.4401 (11)	O3—C25	1.4418 (12)
O2—C5	1.3601 (12)	O4—C21	1.3650 (12)
O2—C10	1.4325 (12)	O4—C26	1.4340 (11)
N1—N2	1.2646 (10)	N3—N4	1.2649 (10)
N1—C1	1.4139 (11)	N3—C17	1.4134 (11)
N2—C11	1.4277 (11)	N4—C27	1.4263 (11)
C1—C2	1.3498 (11)	C17—C18	1.3497 (12)
C1—C3	1.4846 (11)	C17—C19	1.4848 (12)
C3—C4	1.3915 (12)	C19—C20	1.3933 (12)
C3—C8	1.4004 (12)	C19—C24	1.4000 (12)
C4—C5	1.4096 (12)	C20—C21	1.4084 (12)
C5—C6	1.3943 (14)	C21—C22	1.3938 (13)

C6—C7	1.3930 (15)	C22—C23	1.3916 (15)
C6—H6	0.9500	C22—H22	0.9500
C7—C8	1.3869 (13)	C23—C24	1.3863 (14)
C7—H7	0.9500	C23—H23	0.9500
C8—H8	0.9500	C24—H24	0.9500
C9—H9A	0.9800	C25—H25A	0.9800
C9—H9B	0.9800	C25—H25B	0.9800
C9—H9C	0.9800	C25—H25C	0.9800
C10—H10A	0.9800	C26—H26A	0.9800
C10—H10B	0.9800	C26—H26B	0.9800
C10—H10C	0.9800	C26—H26C	0.9800
C11—C16	1.3959 (11)	C27—C32	1.3961 (12)
C11—C12	1.4012 (11)	C27—C28	1.3978 (12)
C12—C13	1.3875 (12)	C28—C29	1.3868 (12)
C12—H12	0.9500	C28—H28	0.9500
C13—C14	1.3942 (12)	C29—C30	1.3929 (13)
C13—H13	0.9500	C29—H29	0.9500
C14—C15	1.3891 (12)	C30—C31	1.3863 (13)
C15—C16	1.3934 (12)	C31—C32	1.3904 (13)
C15—H15	0.9500	C31—H31	0.9500
C16—H16	0.9500	C32—H32	0.9500

C4—O1—C9	117.08 (7)	C20—O3—C25	115.29 (7)
C5—O2—C10	117.18 (8)	C21—O4—C26	116.79 (8)
N2—N1—C1	113.70 (7)	N4—N3—C17	113.56 (7)
N1—N2—C11	113.47 (7)	N3—N4—C27	113.24 (7)
C2—C1—N1	115.71 (7)	C18—C17—N3	115.51 (8)
C2—C1—C3	121.82 (7)	C18—C17—C19	122.16 (8)
N1—C1—C3	122.46 (7)	N3—C17—C19	122.30 (7)
C1—C2—Cl2	123.13 (7)	C17—C18—Cl4	122.85 (7)
C1—C2—Cl1	122.29 (7)	C17—C18—Cl5	122.94 (7)
Cl2—C2—Cl1	114.57 (5)	Cl4—C18—Cl5	114.21 (5)
C4—C3—C8	120.33 (8)	C20—C19—C24	120.27 (8)
C4—C3—C1	118.81 (7)	C20—C19—C17	118.74 (8)
C8—C3—C1	120.86 (8)	C24—C19—C17	120.99 (8)
O1—C4—C3	117.55 (7)	O3—C20—C19	118.06 (7)
O1—C4—C5	122.34 (8)	O3—C20—C21	121.82 (8)
C3—C4—C5	119.88 (8)	C19—C20—C21	119.96 (8)
O2—C5—C6	125.08 (8)	O4—C21—C22	124.62 (8)
O2—C5—C4	115.52 (8)	O4—C21—C20	116.11 (8)
C6—C5—C4	119.40 (9)	C22—C21—C20	119.27 (8)
C7—C6—C5	120.18 (8)	C23—C22—C21	120.24 (8)
C7—C6—H6	119.9	C23—C22—H22	119.9
C5—C6—H6	119.9	C21—C22—H22	119.9
C8—C7—C6	120.65 (9)	C24—C23—C22	120.76 (9)
C8—C7—H7	119.7	C24—C23—H23	119.6
C6—C7—H7	119.7	C22—C23—H23	119.6
C7—C8—C3	119.53 (9)	C23—C24—C19	119.44 (9)

C7—C8—H8	120.2	C23—C24—H24	120.3
C3—C8—H8	120.2	C19—C24—H24	120.3
O1—C9—H9A	109.5	O3—C25—H25A	109.5
O1—C9—H9B	109.5	O3—C25—H25B	109.5
H9A—C9—H9B	109.5	H25A—C25—H25B	109.5
O1—C9—H9C	109.5	O3—C25—H25C	109.5
H9A—C9—H9C	109.5	H25A—C25—H25C	109.5
H9B—C9—H9C	109.5	H25B—C25—H25C	109.5
O2—C10—H10A	109.5	O4—C26—H26A	109.5
O2—C10—H10B	109.5	O4—C26—H26B	109.5
H10A—C10—H10B	109.5	H26A—C26—H26B	109.5
O2—C10—H10C	109.5	O4—C26—H26C	109.5
H10A—C10—H10C	109.5	H26A—C26—H26C	109.5
H10B—C10—H10C	109.5	H26B—C26—H26C	109.5
C16—C11—C12	120.20 (7)	C32—C27—C28	120.14 (8)
C16—C11—N2	115.60 (7)	C32—C27—N4	115.82 (8)
C12—C11—N2	124.20 (7)	C28—C27—N4	123.99 (8)
C13—C12—C11	119.76 (8)	C29—C28—C27	119.81 (8)
C13—C12—H12	120.1	C29—C28—H28	120.1
C11—C12—H12	120.1	C27—C28—H28	120.1
C12—C13—C14	119.25 (8)	C28—C29—C30	119.25 (8)
C12—C13—H13	120.4	C28—C29—H29	120.4
C14—C13—H13	120.4	C30—C29—H29	120.4
C15—C14—C13	121.82 (8)	C31—C30—C29	121.72 (8)
C15—C14—Cl3	118.73 (7)	C31—C30—Cl6	119.16 (7)
C13—C14—Cl3	119.44 (7)	C29—C30—Cl6	119.09 (7)
C14—C15—C16	118.62 (8)	C30—C31—C32	118.77 (8)
C14—C15—H15	120.7	C30—C31—H31	120.6
C16—C15—H15	120.7	C32—C31—H31	120.6
C15—C16—C11	120.35 (8)	C31—C32—C27	120.30 (8)
C15—C16—H16	119.8	C31—C32—H32	119.8
C11—C16—H16	119.8	C27—C32—H32	119.8

C1—N1—N2—C11	−179.49 (7)	C17—N3—N4—C27	176.47 (7)
N2—N1—C1—C2	−175.87 (7)	N4—N3—C17—C18	170.57 (8)
N2—N1—C1—C3	4.67 (11)	N4—N3—C17—C19	−11.33 (12)
N1—C1—C2—Cl2	1.60 (11)	N3—C17—C18—Cl4	177.08 (6)
C3—C1—C2—Cl2	−178.94 (6)	C19—C17—C18—Cl4	−1.02 (13)
N1—C1—C2—Cl1	−177.06 (6)	N3—C17—C18—Cl5	−2.27 (12)
C3—C1—C2—Cl1	2.41 (12)	C19—C17—C18—Cl5	179.62 (7)
C2—C1—C3—C4	−108.12 (10)	C18—C17—C19—C20	112.01 (10)
N1—C1—C3—C4	71.31 (10)	N3—C17—C19—C20	−65.97 (11)
C2—C1—C3—C8	72.24 (11)	C18—C17—C19—C24	−67.47 (12)
N1—C1—C3—C8	−108.33 (10)	N3—C17—C19—C24	114.55 (10)
C9—O1—C4—C3	−121.98 (8)	C25—O3—C20—C19	119.91 (8)
C9—O1—C4—C5	63.47 (11)	C25—O3—C20—C21	−64.64 (10)
C8—C3—C4—O1	−173.36 (8)	C24—C19—C20—O3	177.05 (8)
C1—C3—C4—O1	7.00 (11)	C17—C19—C20—O3	−2.43 (11)

C8—C3—C4—C5	1.34 (12)	C24—C19—C20—C21	1.52 (12)
C1—C3—C4—C5	−178.31 (7)	C17—C19—C20—C21	−177.96 (8)
C10—O2—C5—C6	0.14 (13)	C26—O4—C21—C22	12.60 (12)
C10—O2—C5—C4	−179.98 (8)	C26—O4—C21—C20	−167.81 (8)
O1—C4—C5—O2	−5.68 (12)	O3—C20—C21—O4	2.16 (12)
C3—C4—C5—O2	179.89 (7)	C19—C20—C21—O4	177.53 (8)
O1—C4—C5—C6	174.21 (8)	O3—C20—C21—C22	−178.23 (8)
C3—C4—C5—C6	−0.23 (12)	C19—C20—C21—C22	−2.87 (12)
O2—C5—C6—C7	178.86 (9)	O4—C21—C22—C23	−178.23 (8)
C4—C5—C6—C7	−1.01 (13)	C20—C21—C22—C23	2.20 (13)
C5—C6—C7—C8	1.15 (14)	C21—C22—C23—C24	−0.17 (14)
C6—C7—C8—C3	−0.04 (14)	C22—C23—C24—C19	−1.20 (14)
C4—C3—C8—C7	−1.20 (13)	C20—C19—C24—C23	0.52 (13)
C1—C3—C8—C7	178.43 (8)	C17—C19—C24—C23	179.99 (8)
N1—N2—C11—C16	−178.41 (7)	N3—N4—C27—C32	170.83 (8)
N1—N2—C11—C12	2.04 (12)	N3—N4—C27—C28	−11.65 (12)
C16—C11—C12—C13	0.52 (12)	C32—C27—C28—C29	−0.28 (13)
N2—C11—C12—C13	−179.95 (8)	N4—C27—C28—C29	−177.70 (8)
C11—C12—C13—C14	−0.45 (12)	C27—C28—C29—C30	0.17 (13)
C12—C13—C14—C15	0.06 (13)	C28—C29—C30—C31	−0.33 (14)
C12—C13—C14—Cl3	−179.04 (6)	C28—C29—C30—Cl6	178.02 (7)
C13—C14—C15—C16	0.28 (13)	C29—C30—C31—C32	0.58 (14)
Cl3—C14—C15—C16	179.39 (7)	Cl6—C30—C31—C32	−177.77 (7)
C14—C15—C16—C11	−0.22 (13)	C30—C31—C32—C27	−0.68 (14)
C12—C11—C16—C15	−0.17 (13)	C28—C27—C32—C31	0.54 (14)
N2—C11—C16—C15	−179.74 (8)	N4—C27—C32—C31	178.16 (8)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*C*···O2	0.98	2.32	2.9059 (12)	117
C10—H10*C*···O3$^{\rm i}$	0.98	2.65	3.3241 (13)	126
C12—H12···O1$^{\rm ii}$	0.95	2.66	3.2919 (11)	125
C25—H25*B*···O4	0.98	2.33	2.9226 (12)	118
C25—H25*C*···N4	0.98	2.58	3.2210 (13)	124
C31—H31···Cl2$^{\rm iii}$	0.95	2.87	3.7991 (10)	166

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