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(4*S*,5*R*)-3-(4-Chlorophenyl)-5-(4-methoxyphenyl)-4-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazole

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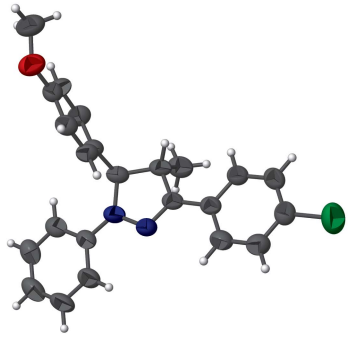
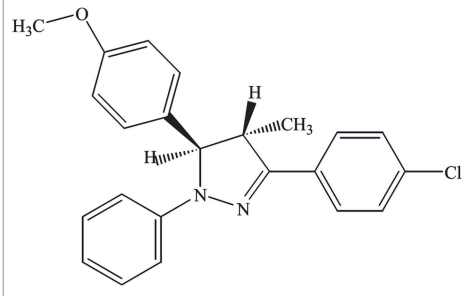
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{23}H_{21}ClN_2O$, was obtained *via* the condensation of *trans* anethole [systematic name: (*E*)-1-Methoxy-4-(1-propenyl)benzene] with diarylnitrilimine. In the molecule, the pyrazole ring adopts a twisted conformation. Dihedral angles between the pyrazole group and the three aromatic subunits (chlorophenyl, methoxyphenyl and phenyl) are 9.44 (14), 83.14 (1) and 20.86 (15)°, respectively. In the crystal, no classic hydrogen bonds are found; however C—H$\cdots\pi$ interactions link the molecules into chains parallel to the *c* axis.

3D view



Chemical scheme



Structure description

Trans-anethole is the active ingredient of the anise essential oil and the source of the anise scent. It has anticarcinogenic (Chainy *et al.*, 2000), antigenotoxic (Abraham *et al.*, 2001), gastroprotective and anti-oxidative (Freire *et al.*, 2005), antithrombotic (Tognolini *et al.*, 2007), antimicrobial and antiviral (Astani *et al.*, 2011) properties. The double bond in the aromatic α position confers some reactivity. In this work, we focused our efforts on the preparation of new heterocyclic systems by the 1,3-dipolar cycloaddition reaction from *trans*-anethole and diarylnitrilimine. The condensation of *trans*-anethole with diarylnitrilimine generated *in situ* by the action of triethylamine on *N*-phenylarylohydrazonoyl chloride (Huisgen *et al.*, 1962) is carried out in dichloromethane at room temperature. The obtained residue was purified by column chromatography on silica gel and the adduct was isolated in a satisfactory yield.

The structure of this new product (Fig. 1) was determined using its single-crystal X-ray diffraction data. The pyrazole ring has a twist conformation as indicated by the total

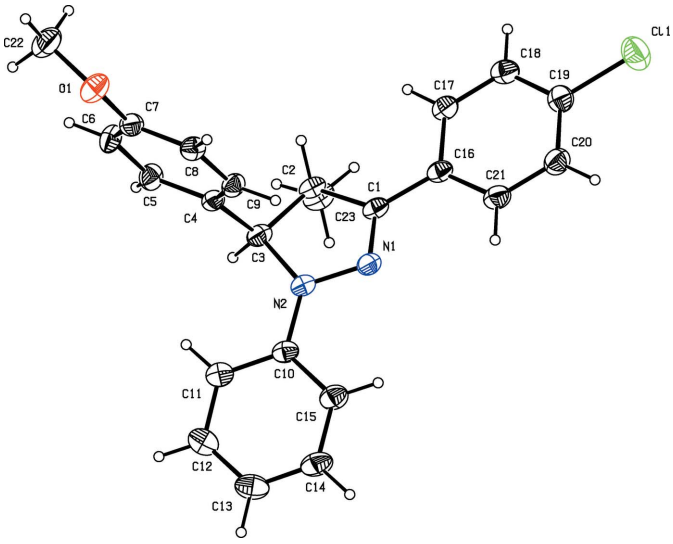


Figure 1
The molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

puckering amplitude Q_T =0.158 (2) Å and φ =86.1 (8)°. The dihedral angles between the five-membered ring and the chlorophenyl, methoxyphenyl and phenyl rings are 9.44 (14), 83.14 (1) and 20.86 (15)°, respectively. The crystal structure features C—H···π interactions (Table 1), which link the molecules into chains parallel to the *c* axis as shown in Fig. 2.

Synthesis and crystallization

Triethylamine (9 mmol) dissolved in dichloromethane (5 mL) was added dropwise to a solution of *trans*-anethole (6.74 mmol) and the precursor diarylnitrilimine (6.74 mmol) contained in a three-necked flask in dichloromethane (15 mL).

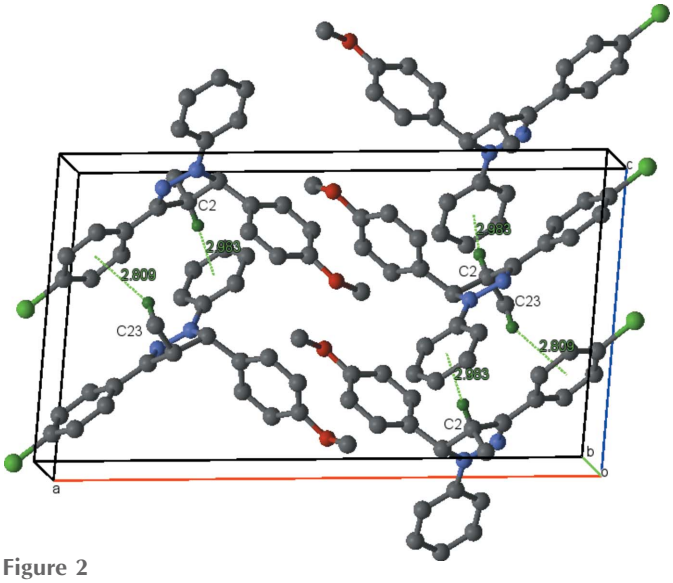


Figure 2
Packing of the title compound showing molecules interconnected by C—H···π interactions and forming types parallel to the *c*-axis direction.

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

*Cg*3 and *Cg*4 are the centroids of the C10–C15 and C16–C21 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···*Cg*3^{i}	0.98	2.98	3.847 (3)	148
C23—H23*C*···*Cg*4^{ii}	0.96	2.80	3.679 (3)	153

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{23}H_{21}ClN_2O$
M_r	376.87
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	298
a, *b*, *c* (Å)	19.564 (16), 9.127 (8), 11.001 (10)
β (°)	94.88 (4)
V (Å^3)	1957 (3)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.21
Crystal size (mm)	0.30 × 0.26 × 0.17
Data collection	
Diffractometer	Bruker X8 APEX
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2003)
T_{min}, T_{max}	0.658, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16805, 3988, 1917
R_{int}	0.065
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.049, 0.123, 0.97
No. of reflections	3988
No. of parameters	246
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.15, −0.22

Computer programs: *APEX2* and *SAINT-Plus* (Bruker, 2009), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

After stirring for one day at room temperature, the mixture was washed several times with water (20 mL). The organic layers were separated, dried by anhydrous sodium sulfate, filtered and evaporated. The residue was purified in a silica-gel column (eluent: hexane/ethyl acetate 2/98), giving the title compound in 54% yield.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161022 [doi:10.1107/S2414314616010221]

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Crystal data

$C_{23}H_{21}ClN_2O$
M_r = 376.87
Monoclinic, $P2_1/c$
a = 19.564 (16) Å
b = 9.127 (8) Å
c = 11.001 (10) Å
β = 94.88 (4)°
V = 1957 (3) Å^3
Z = 4
$F(000)$ = 792
D_x = 1.279 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3988 reflections
θ = 2.5–26.4°
μ = 0.21 mm^{-1}
T = 298 K
Prism, colourless
0.30 × 0.26 × 0.17 mm

Data collection

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.658, T_{max} = 0.747
16805 measured reflections
3988 independent reflections
1917 reflections with $I > 2\sigma(I)$
R_{int} = 0.065
θ_{max} = 26.4°, θ_{min} = 2.5°
h = −24→24
k = −11→11
l = −7→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.123
S = 0.97
3988 reflections
246 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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_{iso}*/U_{eq}
Cl1	−0.04749 (4)	0.25816 (8)	0.48890 (8)	0.0981 (3)
O1	0.51903 (9)	0.34290 (18)	0.41122 (18)	0.0765 (5)
N2	0.25023 (10)	0.4231 (2)	0.05057 (19)	0.0617 (6)
N1	0.19177 (9)	0.43689 (19)	0.10970 (18)	0.0553 (5)
C4	0.35035 (11)	0.3054 (2)	0.1608 (2)	0.0485 (6)
C1	0.18069 (12)	0.3154 (2)	0.1641 (2)	0.0522 (6)
C10	0.26488 (12)	0.5215 (2)	−0.0399 (2)	0.0521 (6)
C3	0.28620 (12)	0.2843 (2)	0.0788 (2)	0.0554 (6)
H3	0.2971	0.2364	0.0030	0.066*
C8	0.41134 (12)	0.4210 (2)	0.3330 (2)	0.0553 (6)
H8	0.4138	0.4934	0.3927	0.066*
C9	0.35455 (12)	0.4104 (2)	0.2521 (2)	0.0539 (6)
H9	0.3181	0.4747	0.2584	0.065*
C2	0.23065 (11)	0.1962 (2)	0.1382 (2)	0.0551 (6)
H2	0.2502	0.1530	0.2150	0.066*
C7	0.46469 (12)	0.3248 (2)	0.3262 (2)	0.0537 (6)
C18	0.06354 (13)	0.1616 (3)	0.3852 (3)	0.0634 (7)
H18	0.0594	0.0769	0.4310	0.076*
C5	0.40490 (13)	0.2124 (2)	0.1551 (2)	0.0607 (7)
H5	0.4035	0.1421	0.0937	0.073*
C19	0.01805 (13)	0.2738 (3)	0.3930 (3)	0.0648 (7)
C16	0.12361 (12)	0.3001 (2)	0.2407 (2)	0.0523 (6)
C17	0.11574 (12)	0.1745 (2)	0.3091 (2)	0.0590 (7)
H17	0.1463	0.0973	0.3036	0.071*
C11	0.32179 (13)	0.5030 (3)	−0.1049 (2)	0.0584 (6)
H11	0.3523	0.4269	−0.0847	0.070*
C15	0.22128 (13)	0.6379 (2)	−0.0700 (2)	0.0657 (7)
H15	0.1835	0.6542	−0.0259	0.079*
C21	0.07674 (13)	0.4117 (3)	0.2509 (2)	0.0646 (7)
H21	0.0806	0.4970	0.2057	0.077*
C6	0.46144 (13)	0.2201 (3)	0.2374 (3)	0.0641 (7)
H6	0.4974	0.1542	0.2327	0.077*
C12	0.33373 (14)	0.5966 (3)	−0.1997 (2)	0.0684 (7)
H12	0.3722	0.5832	−0.2425	0.082*
C23	0.19815 (13)	0.0763 (3)	0.0553 (2)	0.0766 (8)

H23A	0.1622	0.0292	0.0950	0.115*
H23B	0.2324	0.0053	0.0390	0.115*
H23C	0.1794	0.1190	−0.0200	0.115*
C20	0.02443 (13)	0.3997 (3)	0.3264 (3)	0.0689 (7)
H20	−0.0064	0.4763	0.3324	0.083*
C14	0.23385 (15)	0.7297 (3)	−0.1652 (3)	0.0763 (8)
H14	0.2041	0.8071	−0.1850	0.092*
C22	0.56136 (14)	0.2214 (3)	0.4389 (3)	0.0920 (10)
H22A	0.5343	0.1422	0.4666	0.138*
H22B	0.5963	0.2472	0.5018	0.138*
H22C	0.5824	0.1915	0.3672	0.138*
C13	0.28932 (17)	0.7088 (3)	−0.2310 (3)	0.0769 (8)
H13	0.2967	0.7701	−0.2961	0.092*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0884 (6)	0.0939 (5)	0.1166 (8)	−0.0106 (4)	0.0361 (5)	0.0046 (5)
O1	0.0652 (12)	0.0747 (12)	0.0852 (15)	0.0043 (9)	−0.0190 (11)	0.0003 (10)
N2	0.0594 (13)	0.0641 (12)	0.0614 (15)	0.0122 (10)	0.0035 (11)	0.0200 (11)
N1	0.0532 (12)	0.0553 (12)	0.0565 (14)	0.0051 (9)	−0.0015 (10)	0.0106 (10)
C4	0.0522 (15)	0.0453 (12)	0.0479 (15)	0.0079 (11)	0.0034 (12)	0.0062 (12)
C1	0.0551 (15)	0.0484 (13)	0.0500 (16)	0.0001 (11)	−0.0128 (13)	0.0054 (12)
C10	0.0590 (15)	0.0464 (13)	0.0488 (15)	−0.0071 (12)	−0.0073 (12)	0.0029 (12)
C3	0.0636 (16)	0.0502 (13)	0.0512 (16)	0.0115 (12)	−0.0019 (13)	0.0037 (12)
C8	0.0650 (16)	0.0458 (13)	0.0551 (17)	0.0041 (12)	0.0051 (14)	−0.0022 (12)
C9	0.0563 (15)	0.0461 (13)	0.0590 (17)	0.0119 (11)	0.0043 (13)	0.0005 (13)
C2	0.0613 (16)	0.0498 (13)	0.0515 (16)	0.0065 (12)	−0.0105 (12)	0.0071 (12)
C7	0.0523 (16)	0.0533 (14)	0.0548 (17)	−0.0016 (12)	0.0012 (14)	0.0062 (13)
C18	0.0651 (17)	0.0564 (15)	0.0662 (19)	−0.0136 (13)	−0.0082 (15)	0.0092 (13)
C5	0.0636 (17)	0.0606 (15)	0.0587 (18)	0.0132 (13)	0.0096 (14)	−0.0101 (13)
C19	0.0578 (16)	0.0647 (16)	0.071 (2)	−0.0088 (13)	0.0018 (14)	−0.0002 (15)
C16	0.0539 (15)	0.0495 (13)	0.0508 (16)	−0.0022 (11)	−0.0105 (13)	0.0046 (12)
C17	0.0560 (16)	0.0527 (14)	0.0665 (18)	−0.0021 (12)	−0.0061 (14)	0.0061 (13)
C11	0.0680 (17)	0.0523 (14)	0.0532 (16)	−0.0053 (12)	−0.0051 (13)	−0.0035 (13)
C15	0.0741 (18)	0.0476 (14)	0.074 (2)	−0.0006 (13)	−0.0006 (15)	0.0078 (14)
C21	0.0689 (17)	0.0551 (14)	0.0685 (19)	0.0026 (13)	−0.0013 (15)	0.0117 (14)
C6	0.0515 (16)	0.0656 (16)	0.075 (2)	0.0175 (12)	0.0034 (15)	−0.0051 (15)
C12	0.086 (2)	0.0581 (15)	0.0615 (19)	−0.0192 (15)	0.0115 (15)	−0.0076 (15)
C23	0.0889 (19)	0.0564 (15)	0.081 (2)	0.0011 (14)	−0.0101 (16)	−0.0044 (14)
C20	0.0661 (18)	0.0619 (16)	0.078 (2)	0.0083 (13)	0.0034 (16)	0.0054 (15)
C14	0.094 (2)	0.0478 (15)	0.085 (2)	0.0013 (14)	−0.0043 (18)	0.0201 (16)
C22	0.071 (2)	0.098 (2)	0.103 (3)	0.0150 (17)	−0.0181 (18)	0.0142 (19)
C13	0.109 (2)	0.0524 (16)	0.069 (2)	−0.0153 (16)	0.0058 (18)	0.0062 (15)

Geometric parameters (Å, º)

Cl1—C19	1.734 (3)	C5—C6	1.370 (3)
O1—C7	1.365 (3)	C5—H5	0.9300
O1—C22	1.402 (3)	C19—C20	1.373 (3)
N2—N1	1.369 (2)	C16—C21	1.382 (3)
N2—C10	1.389 (3)	C16—C17	1.387 (3)
N2—C3	1.469 (3)	C17—H17	0.9300
N1—C1	1.287 (3)	C11—C12	1.383 (3)
C4—C5	1.369 (3)	C11—H11	0.9300
C4—C9	1.386 (3)	C15—C14	1.380 (3)
C4—C3	1.495 (3)	C15—H15	0.9300
C1—C16	1.462 (3)	C21—C20	1.377 (3)
C1—C2	1.506 (3)	C21—H21	0.9300
C10—C11	1.384 (3)	C6—H6	0.9300
C10—C15	1.385 (3)	C12—C13	1.368 (3)
C3—C2	1.541 (3)	C12—H12	0.9300
C3—H3	0.9800	C23—H23A	0.9600
C8—C9	1.366 (3)	C23—H23B	0.9600
C8—C7	1.371 (3)	C23—H23C	0.9600
C8—H8	0.9300	C20—H20	0.9300
C9—H9	0.9300	C14—C13	1.368 (4)
C2—C23	1.527 (3)	C14—H14	0.9300
C2—H2	0.9800	C22—H22A	0.9600
C7—C6	1.365 (3)	C22—H22B	0.9600
C18—C19	1.365 (3)	C22—H22C	0.9600
C18—C17	1.380 (3)	C13—H13	0.9300
C18—H18	0.9300		
C7—O1—C22	117.7 (2)	C20—C19—Cl1	119.9 (2)
N1—N2—C10	120.85 (19)	C21—C16—C17	117.4 (2)
N1—N2—C3	112.56 (18)	C21—C16—C1	121.4 (2)
C10—N2—C3	125.8 (2)	C17—C16—C1	121.2 (2)
C1—N1—N2	108.79 (18)	C18—C17—C16	121.5 (2)
C5—C4—C9	117.6 (2)	C18—C17—H17	119.3
C5—C4—C3	120.7 (2)	C16—C17—H17	119.3
C9—C4—C3	121.5 (2)	C12—C11—C10	120.6 (2)
N1—C1—C16	121.2 (2)	C12—C11—H11	119.7
N1—C1—C2	113.4 (2)	C10—C11—H11	119.7
C16—C1—C2	125.4 (2)	C14—C15—C10	120.1 (3)
C11—C10—C15	118.5 (2)	C14—C15—H15	120.0
C11—C10—N2	121.0 (2)	C10—C15—H15	120.0
C15—C10—N2	120.5 (2)	C20—C21—C16	121.5 (2)
N2—C3—C4	112.25 (19)	C20—C21—H21	119.3
N2—C3—C2	101.37 (18)	C16—C21—H21	119.3
C4—C3—C2	113.40 (19)	C7—C6—C5	119.7 (2)
N2—C3—H3	109.8	C7—C6—H6	120.2
C4—C3—H3	109.8	C5—C6—H6	120.2

C2—C3—H3	109.8	C13—C12—C11	120.5 (3)
C9—C8—C7	120.0 (2)	C13—C12—H12	119.7
C9—C8—H8	120.0	C11—C12—H12	119.7
C7—C8—H8	120.0	C2—C23—H23A	109.5
C8—C9—C4	121.0 (2)	C2—C23—H23B	109.5
C8—C9—H9	119.5	H23A—C23—H23B	109.5
C4—C9—H9	119.5	C2—C23—H23C	109.5
C1—C2—C23	112.7 (2)	H23A—C23—H23C	109.5
C1—C2—C3	101.28 (17)	H23B—C23—H23C	109.5
C23—C2—C3	113.2 (2)	C19—C20—C21	119.7 (2)
C1—C2—H2	109.8	C19—C20—H20	120.2
C23—C2—H2	109.8	C21—C20—H20	120.2
C3—C2—H2	109.8	C13—C14—C15	121.2 (3)
C6—C7—O1	124.2 (2)	C13—C14—H14	119.4
C6—C7—C8	119.9 (2)	C15—C14—H14	119.4
O1—C7—C8	115.9 (2)	O1—C22—H22A	109.5
C19—C18—C17	119.6 (2)	O1—C22—H22B	109.5
C19—C18—H18	120.2	H22A—C22—H22B	109.5
C17—C18—H18	120.2	O1—C22—H22C	109.5
C4—C5—C6	121.8 (2)	H22A—C22—H22C	109.5
C4—C5—H5	119.1	H22B—C22—H22C	109.5
C6—C5—H5	119.1	C12—C13—C14	119.1 (3)
C18—C19—C20	120.3 (2)	C12—C13—H13	120.4
C18—C19—Cl1	119.7 (2)	C14—C13—H13	120.4

Hydrogen-bond geometry (Å, º)

*Cg*3 and *Cg*4 are the centroids of the C10–C15 and C16–C21 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···*Cg*3^{i}	0.98	2.98	3.847 (3)	148
C23—H23*C*···*Cg*4^{ii}	0.96	2.80	3.679 (3)	153

Symmetry codes: (i) *x*, −*y*−1/2, *z*−1/2; (ii) *x*, −*y*−1/2, *z*−3/2.