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25,27-(3,6,9-Trioxaundecane-1,11-dioxy)-26,28-{3-[4-(tricyanoethylene)phenyl]-3-azapentane-1,5-dioxy}calix[4]arene dichloromethane monosolvate

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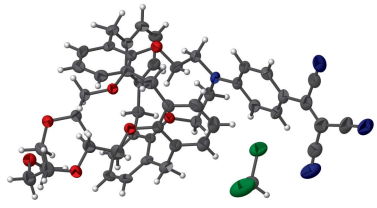
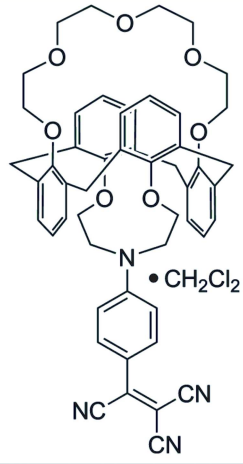
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{51}H_{48}N_2O_7$, was synthesized by the reaction of 25,27-(3,6,9-trioxaundecane-1,11-dioxy)-26,28-(3-phenyl)-3-azapentane-1,5-dioxy)-calix[4]arene with tetracyanoethylene in dry DMF. The compound has a 1,3-alternate conformation with an oxo-crown-5 unit and an aza-crown-3 unit with a nitrogen atom connecting tricyanoethylenephenyl group as a chromophore. Pairs of benzene rings of the calixarene are facing one another. Three of the four oxygen atoms connected to a benzene have *endo*-conformations while the other is *exo*. The oxo-crown-5 system has a *t*–*g*–*g*–*t* conformation. The dichloromethane solvent molecule is linked to the main molecule by a C—H···Cl hydrogen bond. In the crystal, C—H···O, C—H···Cl hydrogen bonds and C—H···π(ring) interactions are observed.

3D view



Chemical scheme



Structure description

Many 1,3-calix[4]arene compounds with crown, aza-crown (Kim *et al.*, 2000) and thia-crown (Sim *et al.*, 2002) linkages have been synthesized and reported. In this paper, we have synthesized a macrocyclic calix[4]arene compound containing oxygen and nitrogen atoms as mixed-donors. Further addition of tetracyanoethylene in DMF solvent connects a chromophore in the *para* position of the N-bound phenyl ring to give the title compound which has potential applications as a chromogenic indicator.

The structure of the title compound is shown in Fig. 1, the calix[4]arene unit has a 1,3-alternate conformation with an oxo-crown-5 ring and an aza-crown-3 ring with a nitrogen atom linked to a tricyanoethylene group. Four of the benzene rings (C9–C14, C16–C21, C23–C28 and C30—C35 with centroids *Cg*1–*Cg*4, respectively) in the calix[4]arene are

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

D—H···A	D—H	H···A	D···A	D—H···A
C22—H22A···O7^{i}	0.99	2.56	3.517 (4)	164
C39—H39A···O6	0.99	2.27	3.116 (4)	143
C46—H46···Cl1	0.95	2.83	3.738 (4)	161
C52—H52B···O3^{ii}	0.99	2.28	3.127 (5)	143
C52—H52B···O4^{ii}	0.99	2.44	3.267 (5)	140
C7—H7A···Cg4	0.99	2.67	3.544 (3)	147
C7—H7B···Cg2	0.99	3.00	3.827 (4)	142
C11—H11···Cg4^{iii}	0.95	2.70	3.615 (3)	161
C40—H40A···Cg1	0.99	2.72	3.630 (4)	153
C42—H42···Cg2^{i}	0.95	2.88	3.653 (4)	139
C52—H52A···Cg1^{iv}	0.99	2.80	3.790 (5)	176

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

arranged to face one another in pairs. The dihedral angles between the planes of facing rings are 64.82 (12)° for $Cg1$–$Cg3$ and 42.28 (12)° for $Cg2$–$Cg4$. Three of the four oxygen atoms (O1, O5, O6) bound to benzene rings have *endo*-conformations while the other one (O7) is *exo*. The geometric conformation of the oxo-crown-5 is *t*-*g*-*g*-*t* conformation and the torsion angles are O1—C1—C2—O2 = 165.7 (3), O2—C3—C4—O3 = −69.1 (4), O3—C5—C6—O4 = 59.0 (4), O4—C7—C8—O5 = 175.1 (2)°, respectively.

In the crystal structure several different types of hydrogen bonds are observed. The dichloromethane solvent molecule is linked to the main molecule by a C—H···Cl hydrogen bond and a variety of C—H···O hydrogen bonds also stabilize the packing (Fig. 2, Table 1). In addition, several weak intermolecular C—H···π(ring) interactions are also found, Table 1.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{52}H_{50}Cl_2N_4O_7$
M_r	913.86
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	200
a, b, c (Å)	13.702 (3), 11.349 (2), 28.538 (6)
β (°)	92.999 (5)
V (Å^3)	4431.4 (15)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.21
Crystal size (mm)	0.47 × 0.19 × 0.17
Data collection	
Diffractometer	Bruker CCD area detector
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	32433, 11032, 4410
R_{int}	0.087
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.061, 0.175, 0.88
No. of reflections	11032
No. of parameters	586
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.77, −0.76

Computer programs: *SMART* and *SAINT* (Bruker, 2000), *SHELXS97* (Sheldrick, 2008), *SHELXL2018/1* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip 2010).

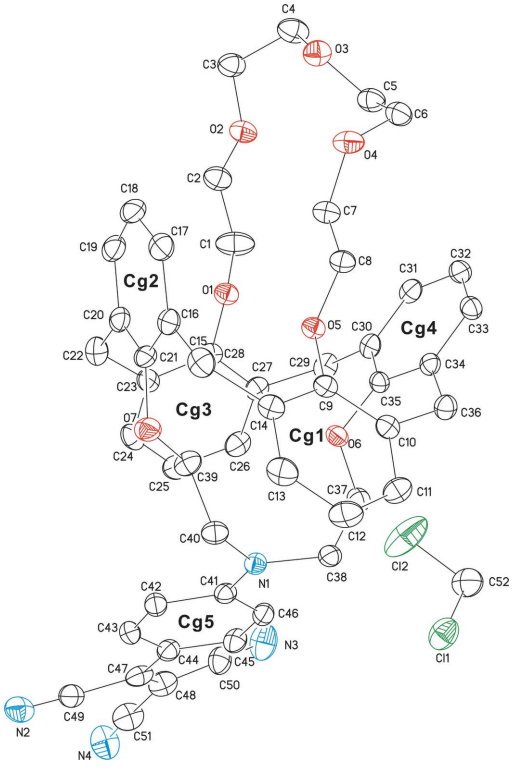


Figure 1
The structure of the title compound with displacement ellipsoids shown at the 30% probability level. H atoms are omitted for clarity.

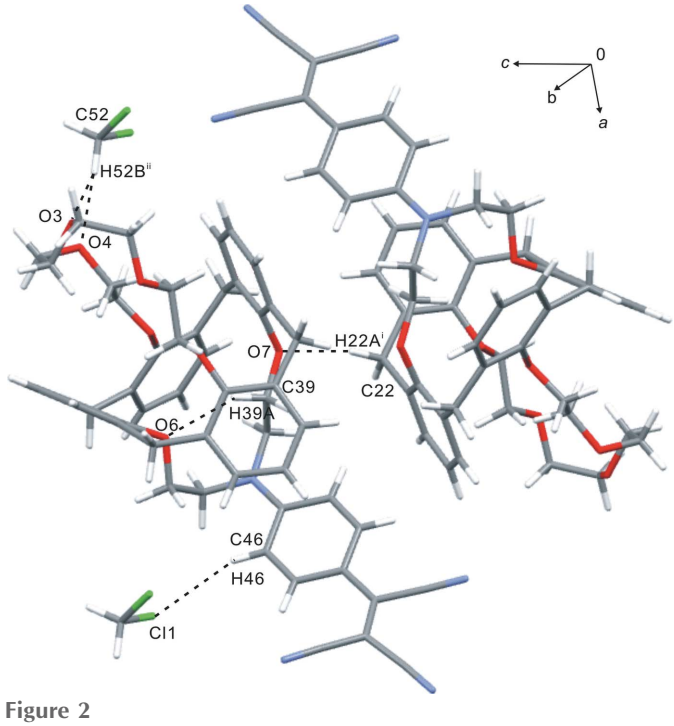


Figure 2
Crystal packing of the title compound with intramolecular and intermolecular C—H···O hydrogen bonds, and C—H···Cl hydrogen bonds drawn as dotted lines. [symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y, z$.]

Synthesis and crystallization

To a refluxing solution of 25,27-(3,6,9-trioxaundecane-1,11-dioxy)-26,28-(3-phenyl)-3-aza-pentane-1,5-dioxy)calix[4]-arene (110 mg, 0.0772 mmol) in dry DMF (15 ml) a solution of tetracyanoethylene (24.1 mg, 0.184 mmol) in dry DMF (15 ml) was added dropwise. The mixture was stirred and refluxed for 24 h then cooled to room temperature. The solvent was removed under reduced pressure. The residue was neutralized with 10% hydrochloric acid and extracted with dichloromethane. The organic layer was washed three times with water and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residue was recrystallized from dichloromethane-hexane (1:2) to give the title compound in 48% yield as red solid. Single crystals suitable for X-ray diffraction were obtained by evaporation of the dichloromethane/hexane solution.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. One reflection (002) with F_o <<< F_c that was likely to have been obscured by the beamstop was omitted from the final rounds of refinement.

Acknowledgements

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full crystallographic data

IUCrData (2019). **4**, x190026 [https://doi.org/10.1107/S2414314619000269]

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Jae Myoung Lee, Sung Baek Kim, Wonbo Sim and Jai Young Lee

(I)

Crystal data

$C_{52}H_{50}Cl_2N_4O_7$
M_r = 913.86
Monoclinic, $P2_1/n$
a = 13.702 (3) Å
b = 11.349 (2) Å
c = 28.538 (6) Å
β = 92.999 (5)°
V = 4431.4 (15) Å^3
Z = 4
$F(000)$ = 1920
D_x = 1.370 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5252 reflections
θ = 2.3–23.1°
μ = 0.21 mm^{-1}
T = 200 K
Rod, brown
0.47 × 0.19 × 0.17 mm

Data collection

Bruker CCD area detector diffractometer
phi and ω scans
32433 measured reflections
11032 independent reflections
4410 reflections with $I > 2\sigma(I)$
R_{int} = 0.087
θ_{max} = 28.3°, θ_{min} = 1.6°
h = −18→17
k = −14→15
l = −33→38

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.175
S = 0.88
11032 reflections
586 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.77 e Å^{-3}
$\Delta\rho_{min}$ = −0.76 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_{iso}*/U_{eq}
O1	0.48433 (15)	0.88386 (18)	0.59186 (7)	0.0361 (5)
C1	0.4540 (3)	1.0024 (3)	0.59431 (17)	0.0658 (12)
H1A	0.473168	1.044717	0.565901	0.079*
H1B	0.487356	1.040464	0.621933	0.079*
C2	0.3478 (2)	1.0116 (3)	0.59798 (13)	0.0465 (9)
H2A	0.313920	0.993538	0.567324	0.056*
H2B	0.325545	0.954656	0.621429	0.056*
O2	0.32579 (15)	1.1271 (2)	0.61171 (8)	0.0440 (6)
C3	0.2253 (2)	1.1481 (3)	0.61839 (12)	0.0490 (10)
H3A	0.186147	1.082751	0.604179	0.059*
H3B	0.205065	1.221792	0.602063	0.059*
C4	0.2046 (3)	1.1583 (3)	0.66927 (13)	0.0525 (10)
H4A	0.249526	1.217130	0.684260	0.063*
H4B	0.137001	1.187194	0.671953	0.063*
O3	0.21570 (16)	1.0492 (2)	0.69382 (8)	0.0459 (6)
C5	0.3041 (2)	1.0355 (3)	0.72114 (12)	0.0445 (9)
H5A	0.314182	1.103893	0.742378	0.053*
H5B	0.359717	1.031509	0.700428	0.053*
C6	0.2991 (3)	0.9252 (3)	0.74911 (12)	0.0446 (9)
H6A	0.360848	0.916718	0.768412	0.054*
H6B	0.245433	0.932876	0.770841	0.054*
O4	0.28367 (15)	0.8206 (2)	0.72218 (8)	0.0449 (6)
C7	0.3642 (2)	0.7856 (3)	0.69579 (12)	0.0380 (8)
H7A	0.418948	0.841749	0.701204	0.046*
H7B	0.344795	0.785831	0.661891	0.046*
C8	0.3964 (2)	0.6637 (3)	0.71071 (11)	0.0345 (8)
H8A	0.422500	0.663818	0.743731	0.041*
H8B	0.341166	0.607599	0.707593	0.041*
O5	0.47082 (14)	0.63263 (17)	0.67990 (7)	0.0305 (5)
C9	0.5168 (2)	0.5262 (3)	0.68895 (11)	0.0301 (7)
C10	0.5995 (2)	0.5230 (3)	0.71971 (11)	0.0323 (7)
C11	0.6485 (2)	0.4168 (3)	0.72554 (12)	0.0402 (8)
H11	0.704841	0.412996	0.746347	0.048*
C12	0.6175 (3)	0.3167 (3)	0.70188 (13)	0.0477 (9)
H12	0.652466	0.244907	0.706233	0.057*
C13	0.5350 (3)	0.3215 (3)	0.67164 (12)	0.0452 (9)
H13	0.513104	0.252020	0.655775	0.054*
C14	0.4838 (2)	0.4258 (3)	0.66415 (11)	0.0352 (8)
C15	0.3929 (2)	0.4231 (3)	0.63127 (12)	0.0428 (9)
H15A	0.400438	0.357074	0.609100	0.051*
H15B	0.336773	0.403617	0.650334	0.051*
C16	0.3653 (2)	0.5309 (3)	0.60265 (11)	0.0364 (8)
C17	0.2755 (2)	0.5848 (3)	0.60848 (12)	0.0448 (9)
H17	0.232445	0.553066	0.630289	0.054*
C18	0.2481 (2)	0.6841 (3)	0.58281 (13)	0.0484 (10)

H18	0.186598	0.720249	0.586805	0.058*
C19	0.3106 (2)	0.7296 (3)	0.55168 (12)	0.0444 (9)
H19	0.291156	0.797981	0.534397	0.053*
C20	0.4012 (2)	0.6802 (3)	0.54421 (11)	0.0376 (8)
C21	0.4262 (2)	0.5775 (3)	0.56946 (11)	0.0344 (8)
C22	0.4635 (2)	0.7392 (3)	0.50822 (12)	0.0458 (9)
H22A	0.481295	0.678155	0.485417	0.055*
H22B	0.421683	0.797356	0.490817	0.055*
C23	0.5566 (2)	0.8016 (3)	0.52496 (11)	0.0374 (8)
C24	0.6381 (3)	0.7916 (3)	0.49817 (12)	0.0451 (9)
H24	0.631938	0.751756	0.468884	0.054*
C25	0.7273 (3)	0.8375 (3)	0.51283 (13)	0.0501 (10)
H25	0.781211	0.832802	0.493324	0.060*
C26	0.7373 (2)	0.8907 (3)	0.55636 (12)	0.0462 (9)
H26	0.799809	0.918470	0.567360	0.055*
C27	0.6584 (2)	0.9045 (3)	0.58440 (11)	0.0381 (8)
C28	0.5666 (2)	0.8654 (3)	0.56683 (11)	0.0344 (8)
C29	0.6756 (2)	0.9639 (3)	0.63151 (11)	0.0425 (9)
H29A	0.647900	1.044262	0.628491	0.051*
H29B	0.747179	0.973149	0.636870	0.051*
C30	0.6379 (2)	0.9109 (3)	0.67575 (11)	0.0332 (8)
C31	0.5974 (2)	0.9863 (3)	0.70836 (12)	0.0383 (8)
H31	0.587314	1.066635	0.700125	0.046*
C32	0.5719 (2)	0.9489 (3)	0.75157 (12)	0.0390 (8)
H32	0.545425	1.002849	0.772989	0.047*
C33	0.5848 (2)	0.8328 (3)	0.76368 (11)	0.0354 (8)
H33	0.567962	0.806936	0.793866	0.042*
C34	0.6221 (2)	0.7523 (3)	0.73269 (10)	0.0297 (7)
C35	0.6484 (2)	0.7930 (3)	0.68874 (10)	0.0297 (7)
C36	0.6384 (2)	0.6270 (3)	0.74840 (11)	0.0355 (8)
H36A	0.611514	0.619968	0.779808	0.043*
H36B	0.709973	0.615904	0.752866	0.043*
O6	0.68096 (14)	0.71007 (18)	0.65733 (7)	0.0341 (5)
C37	0.7835 (2)	0.6905 (3)	0.65861 (12)	0.0388 (8)
H37A	0.811706	0.702400	0.690905	0.047*
H37B	0.814652	0.747182	0.637656	0.047*
C38	0.8027 (2)	0.5656 (3)	0.64274 (10)	0.0362 (8)
H38A	0.873586	0.549893	0.647623	0.043*
H38B	0.768337	0.511117	0.663383	0.043*
O7	0.50936 (15)	0.5116 (2)	0.56247 (8)	0.0423 (6)
C39	0.6018 (2)	0.5671 (3)	0.57037 (12)	0.0411 (9)
H39A	0.597538	0.627658	0.595153	0.049*
H39B	0.620390	0.606875	0.541266	0.049*
C40	0.6792 (2)	0.4773 (3)	0.58519 (12)	0.0382 (8)
H40A	0.660371	0.436594	0.614037	0.046*
H40B	0.684668	0.417613	0.560179	0.046*
N1	0.77344 (16)	0.5368 (2)	0.59395 (9)	0.0319 (6)
C41	0.8290 (2)	0.5708 (3)	0.55829 (11)	0.0326 (7)

C42	0.8062 (2)	0.5400 (3)	0.51092 (11)	0.0376 (8)
H42	0.749996	0.493443	0.503321	0.045*
C43	0.8635 (2)	0.5758 (3)	0.47610 (11)	0.0393 (8)
H43	0.846697	0.552081	0.444783	0.047*
C44	0.9465 (2)	0.6468 (3)	0.48481 (11)	0.0393 (8)
C45	0.9705 (2)	0.6758 (3)	0.53215 (12)	0.0411 (9)
H45	1.026732	0.722454	0.539582	0.049*
C46	0.9146 (2)	0.6382 (3)	0.56743 (11)	0.0375 (8)
H46	0.933765	0.657866	0.598942	0.045*
C47	1.0029 (2)	0.6855 (3)	0.44635 (13)	0.0470 (10)
C48	1.0719 (3)	0.7676 (4)	0.44522 (15)	0.0581 (11)
C49	0.9802 (3)	0.6254 (3)	0.39965 (14)	0.0459 (9)
N2	0.9600 (2)	0.5804 (3)	0.36530 (11)	0.0574 (9)
C50	1.0944 (3)	0.8462 (4)	0.48242 (14)	0.0537 (10)
N3	1.1150 (3)	0.9158 (4)	0.51017 (14)	0.0789 (12)
C51	1.1282 (3)	0.7804 (4)	0.40333 (15)	0.0605 (11)
N4	1.1761 (3)	0.7938 (3)	0.37277 (12)	0.0722 (11)
C52	1.0527 (3)	0.8561 (4)	0.69144 (15)	0.0664 (12)
H52A	1.024202	0.871798	0.721997	0.080*
H52B	1.121211	0.884192	0.693487	0.080*
Cl1	1.05144 (7)	0.70456 (9)	0.68090 (4)	0.0666 (3)
Cl2	0.98752 (10)	0.93430 (12)	0.64778 (6)	0.1190 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0389 (12)	0.0304 (13)	0.0393 (13)	0.0024 (10)	0.0065 (11)	0.0017 (10)
C1	0.059 (2)	0.034 (2)	0.107 (4)	0.012 (2)	0.023 (2)	0.008 (2)
C2	0.051 (2)	0.036 (2)	0.053 (2)	0.0064 (18)	0.0088 (18)	0.0013 (18)
O2	0.0441 (14)	0.0360 (15)	0.0529 (15)	0.0032 (11)	0.0114 (12)	−0.0029 (12)
C3	0.048 (2)	0.049 (2)	0.050 (2)	0.0121 (18)	0.0083 (18)	0.0105 (18)
C4	0.060 (2)	0.043 (2)	0.056 (2)	0.0122 (19)	0.018 (2)	0.0102 (19)
O3	0.0472 (14)	0.0405 (15)	0.0504 (15)	0.0020 (12)	0.0050 (12)	0.0068 (12)
C5	0.043 (2)	0.036 (2)	0.055 (2)	0.0029 (17)	0.0054 (18)	−0.0072 (18)
C6	0.047 (2)	0.044 (2)	0.043 (2)	0.0081 (18)	0.0064 (17)	−0.0045 (18)
O4	0.0344 (12)	0.0363 (14)	0.0645 (16)	0.0021 (11)	0.0087 (12)	−0.0066 (12)
C7	0.0359 (18)	0.033 (2)	0.045 (2)	0.0021 (16)	0.0085 (16)	−0.0015 (16)
C8	0.0313 (17)	0.035 (2)	0.0383 (19)	0.0004 (15)	0.0071 (15)	0.0002 (15)
O5	0.0333 (11)	0.0270 (12)	0.0316 (12)	0.0018 (10)	0.0050 (10)	0.0020 (10)
C9	0.0357 (17)	0.0241 (18)	0.0308 (18)	0.0017 (14)	0.0062 (14)	0.0033 (14)
C10	0.0354 (17)	0.0306 (19)	0.0314 (18)	−0.0011 (15)	0.0058 (15)	0.0020 (15)
C11	0.0372 (18)	0.034 (2)	0.049 (2)	−0.0002 (16)	−0.0005 (16)	0.0095 (17)
C12	0.049 (2)	0.026 (2)	0.069 (3)	0.0032 (17)	0.002 (2)	0.0021 (18)
C13	0.054 (2)	0.025 (2)	0.058 (2)	−0.0033 (17)	0.0061 (19)	−0.0042 (17)
C14	0.0372 (18)	0.0291 (19)	0.040 (2)	−0.0022 (15)	0.0049 (15)	0.0002 (15)
C15	0.045 (2)	0.036 (2)	0.047 (2)	−0.0108 (17)	0.0041 (17)	−0.0040 (17)
C16	0.0300 (17)	0.038 (2)	0.041 (2)	−0.0102 (15)	−0.0037 (15)	−0.0097 (16)
C17	0.0307 (18)	0.056 (3)	0.047 (2)	−0.0125 (18)	0.0012 (16)	−0.0120 (19)

C18	0.0327 (19)	0.051 (3)	0.061 (3)	0.0048 (18)	−0.0093 (18)	−0.018 (2)
C19	0.0391 (19)	0.043 (2)	0.050 (2)	−0.0005 (17)	−0.0109 (18)	−0.0058 (18)
C20	0.0364 (18)	0.038 (2)	0.037 (2)	−0.0023 (16)	−0.0076 (15)	−0.0061 (16)
C21	0.0250 (16)	0.038 (2)	0.040 (2)	−0.0003 (15)	−0.0026 (15)	−0.0063 (16)
C22	0.055 (2)	0.045 (2)	0.037 (2)	−0.0033 (19)	−0.0032 (18)	0.0000 (17)
C23	0.047 (2)	0.035 (2)	0.0304 (19)	0.0063 (17)	0.0048 (16)	0.0053 (15)
C24	0.067 (2)	0.037 (2)	0.032 (2)	0.0070 (19)	0.0072 (18)	0.0041 (16)
C25	0.047 (2)	0.061 (3)	0.044 (2)	0.006 (2)	0.0137 (19)	0.017 (2)
C26	0.041 (2)	0.053 (2)	0.045 (2)	−0.0009 (18)	0.0030 (18)	0.0147 (19)
C27	0.0393 (19)	0.035 (2)	0.040 (2)	0.0003 (16)	0.0023 (16)	0.0098 (16)
C28	0.0378 (18)	0.033 (2)	0.0332 (19)	0.0013 (15)	0.0065 (15)	0.0085 (15)
C29	0.0427 (19)	0.041 (2)	0.044 (2)	−0.0087 (17)	−0.0025 (17)	0.0061 (17)
C30	0.0342 (17)	0.0288 (19)	0.0361 (19)	−0.0099 (15)	−0.0044 (15)	−0.0001 (15)
C31	0.0405 (19)	0.0255 (19)	0.048 (2)	−0.0001 (15)	−0.0110 (17)	−0.0067 (16)
C32	0.0406 (19)	0.036 (2)	0.040 (2)	0.0020 (16)	−0.0028 (16)	−0.0128 (16)
C33	0.0360 (18)	0.038 (2)	0.0327 (18)	−0.0026 (16)	0.0024 (15)	−0.0059 (16)
C34	0.0295 (16)	0.0297 (18)	0.0297 (18)	−0.0028 (14)	−0.0019 (14)	−0.0027 (14)
C35	0.0294 (16)	0.0300 (18)	0.0294 (17)	−0.0018 (14)	0.0001 (14)	−0.0069 (15)
C36	0.0398 (18)	0.034 (2)	0.0324 (18)	−0.0002 (16)	−0.0005 (15)	0.0030 (15)
O6	0.0321 (11)	0.0360 (13)	0.0345 (12)	0.0000 (10)	0.0046 (10)	−0.0080 (10)
C37	0.0346 (18)	0.044 (2)	0.038 (2)	−0.0036 (16)	0.0057 (15)	−0.0058 (16)
C38	0.0350 (17)	0.045 (2)	0.0293 (18)	0.0068 (16)	0.0055 (15)	0.0044 (15)
O7	0.0324 (12)	0.0412 (15)	0.0532 (15)	−0.0013 (11)	0.0018 (11)	−0.0099 (12)
C39	0.0331 (18)	0.035 (2)	0.055 (2)	−0.0057 (16)	−0.0023 (16)	0.0022 (17)
C40	0.0329 (17)	0.037 (2)	0.045 (2)	0.0004 (16)	0.0069 (16)	0.0026 (16)
N1	0.0258 (13)	0.0373 (17)	0.0329 (15)	−0.0023 (12)	0.0046 (12)	0.0016 (12)
C41	0.0277 (16)	0.037 (2)	0.0329 (19)	0.0026 (15)	0.0038 (14)	0.0028 (15)
C42	0.0325 (17)	0.045 (2)	0.035 (2)	−0.0028 (16)	0.0030 (15)	−0.0031 (16)
C43	0.0419 (19)	0.045 (2)	0.0306 (19)	0.0044 (17)	0.0029 (16)	−0.0017 (16)
C44	0.0332 (18)	0.049 (2)	0.036 (2)	0.0038 (17)	0.0050 (15)	0.0055 (17)
C45	0.0301 (17)	0.050 (2)	0.043 (2)	−0.0066 (16)	0.0014 (16)	0.0039 (17)
C46	0.0329 (18)	0.045 (2)	0.0346 (19)	0.0006 (16)	−0.0005 (15)	0.0007 (16)
C47	0.0374 (19)	0.047 (2)	0.057 (3)	0.0109 (18)	0.0050 (18)	0.0151 (19)
C48	0.049 (2)	0.056 (3)	0.069 (3)	0.002 (2)	0.003 (2)	0.007 (2)
C49	0.047 (2)	0.048 (2)	0.044 (2)	0.0080 (19)	0.0081 (19)	0.009 (2)
N2	0.065 (2)	0.066 (2)	0.043 (2)	0.0099 (18)	0.0178 (18)	0.0090 (18)
C50	0.054 (2)	0.064 (3)	0.043 (2)	−0.006 (2)	0.001 (2)	0.007 (2)
N3	0.084 (3)	0.075 (3)	0.076 (3)	−0.030 (2)	−0.014 (2)	0.010 (2)
C51	0.053 (2)	0.064 (3)	0.067 (3)	−0.008 (2)	0.019 (2)	0.021 (2)
N4	0.076 (2)	0.081 (3)	0.061 (2)	−0.029 (2)	0.023 (2)	0.003 (2)
C52	0.054 (2)	0.061 (3)	0.084 (3)	−0.006 (2)	−0.003 (2)	−0.011 (2)
Cl1	0.0621 (6)	0.0577 (7)	0.0781 (8)	−0.0087 (5)	−0.0155 (6)	0.0040 (6)
Cl2	0.0894 (9)	0.0754 (10)	0.1855 (16)	−0.0128 (8)	−0.0567 (10)	0.0420 (10)

Geometric parameters (Å, º)

O1—C28	1.382 (3)	C24—H24	0.9500
O1—C1	1.410 (4)	C25—C26	1.381 (5)

C1—C2	1.468 (5)	C25—H25	0.9500
C1—H1A	0.9900	C26—C27	1.388 (4)
C1—H1B	0.9900	C26—H26	0.9500
C2—O2	1.406 (4)	C27—C28	1.401 (4)
C2—H2A	0.9900	C27—C29	1.512 (4)
C2—H2B	0.9900	C29—C30	1.514 (4)
O2—C3	1.419 (4)	C29—H29A	0.9900
C3—C4	1.498 (5)	C29—H29B	0.9900
C3—H3A	0.9900	C30—C35	1.394 (4)
C3—H3B	0.9900	C30—C31	1.399 (4)
C4—O3	1.426 (4)	C31—C32	1.367 (4)
C4—H4A	0.9900	C31—H31	0.9500
C4—H4B	0.9900	C32—C33	1.372 (4)
O3—C5	1.414 (4)	C32—H32	0.9500
C5—C6	1.489 (5)	C33—C34	1.387 (4)
C5—H5A	0.9900	C33—H33	0.9500
C5—H5B	0.9900	C34—C35	1.401 (4)
C6—O4	1.424 (4)	C34—C36	1.505 (4)
C6—H6A	0.9900	C35—O6	1.389 (3)
C6—H6B	0.9900	C36—H36A	0.9900
O4—C7	1.425 (3)	C36—H36B	0.9900
C7—C8	1.506 (4)	O6—C37	1.421 (3)
C7—H7A	0.9900	C37—C38	1.515 (4)
C7—H7B	0.9900	C37—H37A	0.9900
C8—O5	1.425 (3)	C37—H37B	0.9900
C8—H8A	0.9900	C38—N1	1.466 (4)
C8—H8B	0.9900	C38—H38A	0.9900
O5—C9	1.380 (3)	C38—H38B	0.9900
C9—C10	1.397 (4)	O7—C39	1.422 (3)
C9—C14	1.404 (4)	C39—C40	1.514 (4)
C10—C11	1.385 (4)	C39—H39A	0.9900
C10—C36	1.517 (4)	C39—H39B	0.9900
C11—C12	1.377 (4)	C40—N1	1.467 (4)
C11—H11	0.9500	C40—H40A	0.9900
C12—C13	1.388 (5)	C40—H40B	0.9900
C12—H12	0.9500	N1—C41	1.358 (4)
C13—C14	1.386 (4)	C41—C46	1.413 (4)
C13—H13	0.9500	C41—C42	1.415 (4)
C14—C15	1.520 (4)	C42—C43	1.360 (4)
C15—C16	1.508 (4)	C42—H42	0.9500
C15—H15A	0.9900	C43—C44	1.405 (4)
C15—H15B	0.9900	C43—H43	0.9500
C16—C17	1.393 (4)	C44—C45	1.412 (4)
C16—C21	1.398 (4)	C44—C47	1.443 (5)
C17—C18	1.385 (5)	C45—C46	1.365 (4)
C17—H17	0.9500	C45—H45	0.9500
C18—C19	1.366 (5)	C46—H46	0.9500
C18—H18	0.9500	C47—C48	1.329 (5)

C19—C20	1.389 (4)	C47—C49	1.515 (5)
C19—H19	0.9500	C48—C50	1.408 (6)
C20—C21	1.404 (4)	C48—C51	1.464 (5)
C20—C22	1.524 (4)	C49—N2	1.127 (4)
C21—O7	1.386 (3)	C50—N3	1.144 (5)
C22—C23	1.514 (4)	C51—N4	1.129 (4)
C22—H22A	0.9900	C52—Cl2	1.738 (4)
C22—H22B	0.9900	C52—Cl1	1.746 (4)
C23—C24	1.391 (4)	C52—H52A	0.9900
C23—C28	1.398 (4)	C52—H52B	0.9900
C24—C25	1.373 (5)		

C28—O1—C1	114.9 (3)	C23—C24—H24	119.0
O1—C1—C2	111.6 (3)	C24—C25—C26	119.0 (3)
O1—C1—H1A	109.3	C24—C25—H25	120.5
C2—C1—H1A	109.3	C26—C25—H25	120.5
O1—C1—H1B	109.3	C25—C26—C27	121.6 (3)
C2—C1—H1B	109.3	C25—C26—H26	119.2
H1A—C1—H1B	108.0	C27—C26—H26	119.2
O2—C2—C1	108.3 (3)	C26—C27—C28	118.0 (3)
O2—C2—H2A	110.0	C26—C27—C29	118.2 (3)
C1—C2—H2A	110.0	C28—C27—C29	123.7 (3)
O2—C2—H2B	110.0	O1—C28—C23	118.3 (3)
C1—C2—H2B	110.0	O1—C28—C27	120.5 (3)
H2A—C2—H2B	108.4	C23—C28—C27	121.1 (3)
C2—O2—C3	114.7 (3)	C27—C29—C30	121.4 (3)
O2—C3—C4	112.1 (3)	C27—C29—H29A	107.0
O2—C3—H3A	109.2	C30—C29—H29A	107.0
C4—C3—H3A	109.2	C27—C29—H29B	107.0
O2—C3—H3B	109.2	C30—C29—H29B	107.0
C4—C3—H3B	109.2	H29A—C29—H29B	106.7
H3A—C3—H3B	107.9	C35—C30—C31	116.7 (3)
O3—C4—C3	112.9 (3)	C35—C30—C29	124.6 (3)
O3—C4—H4A	109.0	C31—C30—C29	118.5 (3)
C3—C4—H4A	109.0	C32—C31—C30	122.7 (3)
O3—C4—H4B	109.0	C32—C31—H31	118.7
C3—C4—H4B	109.0	C30—C31—H31	118.7
H4A—C4—H4B	107.8	C31—C32—C33	119.3 (3)
C5—O3—C4	115.6 (3)	C31—C32—H32	120.4
O3—C5—C6	109.0 (3)	C33—C32—H32	120.4
O3—C5—H5A	109.9	C32—C33—C34	121.3 (3)
C6—C5—H5A	109.9	C32—C33—H33	119.4
O3—C5—H5B	109.9	C34—C33—H33	119.4
C6—C5—H5B	109.9	C33—C34—C35	118.3 (3)
H5A—C5—H5B	108.3	C33—C34—C36	119.1 (3)
O4—C6—C5	114.9 (3)	C35—C34—C36	122.5 (3)
O4—C6—H6A	108.5	O6—C35—C30	120.7 (3)
C5—C6—H6A	108.5	O6—C35—C34	117.4 (3)

O4—C6—H6B	108.5	C30—C35—C34	121.8 (3)
C5—C6—H6B	108.5	C34—C36—C10	122.1 (3)
H6A—C6—H6B	107.5	C34—C36—H36A	106.8
C6—O4—C7	114.9 (2)	C10—C36—H36A	106.8
O4—C7—C8	109.3 (3)	C34—C36—H36B	106.8
O4—C7—H7A	109.8	C10—C36—H36B	106.8
C8—C7—H7A	109.8	H36A—C36—H36B	106.6
O4—C7—H7B	109.8	C35—O6—C37	116.1 (2)
C8—C7—H7B	109.8	O6—C37—C38	109.0 (3)
H7A—C7—H7B	108.3	O6—C37—H37A	109.9
O5—C8—C7	105.1 (2)	C38—C37—H37A	109.9
O5—C8—H8A	110.7	O6—C37—H37B	109.9
C7—C8—H8A	110.7	C38—C37—H37B	109.9
O5—C8—H8B	110.7	H37A—C37—H37B	108.3
C7—C8—H8B	110.7	N1—C38—C37	116.7 (3)
H8A—C8—H8B	108.8	N1—C38—H38A	108.1
C9—O5—C8	115.8 (2)	C37—C38—H38A	108.1
O5—C9—C10	119.2 (3)	N1—C38—H38B	108.1
O5—C9—C14	119.0 (3)	C37—C38—H38B	108.1
C10—C9—C14	121.7 (3)	H38A—C38—H38B	107.3
C11—C10—C9	118.1 (3)	C21—O7—C39	118.1 (2)
C11—C10—C36	117.2 (3)	O7—C39—C40	110.5 (3)
C9—C10—C36	124.7 (3)	O7—C39—H39A	109.5
C12—C11—C10	121.6 (3)	C40—C39—H39A	109.5
C12—C11—H11	119.2	O7—C39—H39B	109.5
C10—C11—H11	119.2	C40—C39—H39B	109.5
C11—C12—C13	119.5 (3)	H39A—C39—H39B	108.1
C11—C12—H12	120.2	N1—C40—C39	109.6 (3)
C13—C12—H12	120.2	N1—C40—H40A	109.8
C14—C13—C12	121.3 (3)	C39—C40—H40A	109.8
C14—C13—H13	119.4	N1—C40—H40B	109.8
C12—C13—H13	119.4	C39—C40—H40B	109.8
C13—C14—C9	117.9 (3)	H40A—C40—H40B	108.2
C13—C14—C15	118.1 (3)	C41—N1—C38	120.8 (2)
C9—C14—C15	124.0 (3)	C41—N1—C40	121.7 (3)
C16—C15—C14	119.5 (3)	C38—N1—C40	117.3 (2)
C16—C15—H15A	107.4	N1—C41—C46	120.5 (3)
C14—C15—H15A	107.4	N1—C41—C42	122.8 (3)
C16—C15—H15B	107.4	C46—C41—C42	116.7 (3)
C14—C15—H15B	107.4	C43—C42—C41	121.2 (3)
H15A—C15—H15B	107.0	C43—C42—H42	119.4
C17—C16—C21	118.5 (3)	C41—C42—H42	119.4
C17—C16—C15	119.3 (3)	C42—C43—C44	122.3 (3)
C21—C16—C15	122.2 (3)	C42—C43—H43	118.8
C18—C17—C16	120.7 (3)	C44—C43—H43	118.8
C18—C17—H17	119.7	C43—C44—C45	116.6 (3)
C16—C17—H17	119.7	C43—C44—C47	120.0 (3)
C19—C18—C17	119.4 (3)	C45—C44—C47	123.3 (3)

C19—C18—H18	120.3	C46—C45—C44	121.4 (3)
C17—C18—H18	120.3	C46—C45—H45	119.3
C18—C19—C20	122.8 (3)	C44—C45—H45	119.3
C18—C19—H19	118.6	C45—C46—C41	121.7 (3)
C20—C19—H19	118.6	C45—C46—H46	119.2
C19—C20—C21	116.9 (3)	C41—C46—H46	119.2
C19—C20—C22	117.5 (3)	C48—C47—C44	129.9 (4)
C21—C20—C22	125.5 (3)	C48—C47—C49	114.0 (3)
O7—C21—C16	114.7 (3)	C44—C47—C49	116.0 (3)
O7—C21—C20	123.7 (3)	C47—C48—C50	123.6 (4)
C16—C21—C20	121.6 (3)	C47—C48—C51	119.7 (4)
C23—C22—C20	119.0 (3)	C50—C48—C51	116.7 (4)
C23—C22—H22A	107.6	N2—C49—C47	177.6 (4)
C20—C22—H22A	107.6	N3—C50—C48	174.9 (5)
C23—C22—H22B	107.6	N4—C51—C48	175.6 (5)
C20—C22—H22B	107.6	Cl2—C52—Cl1	112.3 (2)
H22A—C22—H22B	107.0	Cl2—C52—H52A	109.1
C24—C23—C28	117.8 (3)	Cl1—C52—H52A	109.1
C24—C23—C22	118.4 (3)	Cl2—C52—H52B	109.1
C28—C23—C22	123.7 (3)	Cl1—C52—H52B	109.1
C25—C24—C23	121.9 (3)	H52A—C52—H52B	107.9
C25—C24—H24	119.0		

C28—O1—C1—C2	150.1 (3)	C22—C23—C28—C27	169.2 (3)
O1—C1—C2—O2	165.7 (3)	C26—C27—C28—O1	−175.7 (3)
C1—C2—O2—C3	−177.8 (3)	C29—C27—C28—O1	2.4 (5)
C2—O2—C3—C4	106.5 (3)	C26—C27—C28—C23	7.7 (5)
O2—C3—C4—O3	−69.1 (4)	C29—C27—C28—C23	−174.2 (3)
C3—C4—O3—C5	101.0 (3)	C26—C27—C29—C30	−131.7 (3)
C4—O3—C5—C6	172.8 (3)	C28—C27—C29—C30	50.1 (5)
O3—C5—C6—O4	59.0 (4)	C27—C29—C30—C35	47.1 (5)
C5—C6—O4—C7	69.8 (4)	C27—C29—C30—C31	−139.1 (3)
C6—O4—C7—C8	121.0 (3)	C35—C30—C31—C32	2.1 (4)
O4—C7—C8—O5	175.1 (2)	C29—C30—C31—C32	−172.2 (3)
C7—C8—O5—C9	175.7 (2)	C30—C31—C32—C33	−0.9 (5)
C8—O5—C9—C10	−89.2 (3)	C31—C32—C33—C34	−0.9 (5)
C8—O5—C9—C14	95.8 (3)	C32—C33—C34—C35	1.3 (4)
O5—C9—C10—C11	−175.3 (3)	C32—C33—C34—C36	177.7 (3)
C14—C9—C10—C11	−0.4 (4)	C31—C30—C35—O6	175.2 (3)
O5—C9—C10—C36	6.4 (4)	C29—C30—C35—O6	−10.9 (4)
C14—C9—C10—C36	−178.8 (3)	C31—C30—C35—C34	−1.6 (4)
C9—C10—C11—C12	0.1 (5)	C29—C30—C35—C34	172.3 (3)
C36—C10—C11—C12	178.5 (3)	C33—C34—C35—O6	−176.9 (2)
C10—C11—C12—C13	−0.4 (5)	C36—C34—C35—O6	6.9 (4)
C11—C12—C13—C14	1.1 (5)	C33—C34—C35—C30	0.0 (4)
C12—C13—C14—C9	−1.4 (5)	C36—C34—C35—C30	−176.3 (3)
C12—C13—C14—C15	−178.8 (3)	C33—C34—C36—C10	129.1 (3)
O5—C9—C14—C13	176.0 (3)	C35—C34—C36—C10	−54.7 (4)

C10—C9—C14—C13	1.1 (5)	C11—C10—C36—C34	154.3 (3)
O5—C9—C14—C15	−6.8 (4)	C9—C10—C36—C34	−27.4 (5)
C10—C9—C14—C15	178.3 (3)	C30—C35—O6—C37	91.5 (3)
C13—C14—C15—C16	−148.4 (3)	C34—C35—O6—C37	−91.6 (3)
C9—C14—C15—C16	34.3 (5)	C35—O6—C37—C38	152.0 (3)
C14—C15—C16—C17	−119.8 (3)	O6—C37—C38—N1	65.0 (3)
C14—C15—C16—C21	61.7 (4)	C16—C21—O7—C39	−121.7 (3)
C21—C16—C17—C18	−1.6 (5)	C20—C21—O7—C39	61.0 (4)
C15—C16—C17—C18	179.8 (3)	C21—O7—C39—C40	151.5 (3)
C16—C17—C18—C19	−0.3 (5)	O7—C39—C40—N1	−179.0 (3)
C17—C18—C19—C20	0.3 (5)	C37—C38—N1—C41	78.1 (4)
C18—C19—C20—C21	1.7 (5)	C37—C38—N1—C40	−98.0 (3)
C18—C19—C20—C22	179.6 (3)	C39—C40—N1—C41	−78.1 (4)
C17—C16—C21—O7	−173.6 (3)	C39—C40—N1—C38	97.8 (3)
C15—C16—C21—O7	4.9 (4)	C38—N1—C41—C46	−2.2 (4)
C17—C16—C21—C20	3.7 (5)	C40—N1—C41—C46	173.7 (3)
C15—C16—C21—C20	−177.8 (3)	C38—N1—C41—C42	176.8 (3)
C19—C20—C21—O7	173.4 (3)	C40—N1—C41—C42	−7.4 (4)
C22—C20—C21—O7	−4.3 (5)	N1—C41—C42—C43	179.8 (3)
C19—C20—C21—C16	−3.7 (5)	C46—C41—C42—C43	−1.2 (5)
C22—C20—C21—C16	178.5 (3)	C41—C42—C43—C44	−1.3 (5)
C19—C20—C22—C23	111.5 (4)	C42—C43—C44—C45	2.5 (5)
C21—C20—C22—C23	−70.8 (4)	C42—C43—C44—C47	−178.0 (3)
C20—C22—C23—C24	141.0 (3)	C43—C44—C45—C46	−1.1 (5)
C20—C22—C23—C28	−36.5 (5)	C47—C44—C45—C46	179.4 (3)
C28—C23—C24—C25	2.9 (5)	C44—C45—C46—C41	−1.4 (5)
C22—C23—C24—C25	−174.7 (3)	N1—C41—C46—C45	−178.4 (3)
C23—C24—C25—C26	2.9 (5)	C42—C41—C46—C45	2.5 (5)
C24—C25—C26—C27	−3.6 (5)	C43—C44—C47—C48	166.8 (4)
C25—C26—C27—C28	−1.6 (5)	C45—C44—C47—C48	−13.7 (6)
C25—C26—C27—C29	−179.8 (3)	C43—C44—C47—C49	−12.3 (5)
C1—O1—C28—C23	−113.6 (4)	C45—C44—C47—C49	167.2 (3)
C1—O1—C28—C27	69.6 (4)	C44—C47—C48—C50	−8.9 (6)
C24—C23—C28—O1	175.0 (3)	C49—C47—C48—C50	170.3 (4)
C22—C23—C28—O1	−7.5 (5)	C44—C47—C48—C51	171.8 (3)
C24—C23—C28—C27	−8.3 (5)	C49—C47—C48—C51	−9.0 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C22—H22*A*···O7^{i}	0.99	2.56	3.517 (4)	164
C39—H39*A*···O6	0.99	2.27	3.116 (4)	143
C46—H46···Cl1	0.95	2.83	3.738 (4)	161
C52—H52*B*···O3^{ii}	0.99	2.28	3.127 (5)	143
C52—H52*B*···O4^{ii}	0.99	2.44	3.267 (5)	140
C7—H7*A*···*Cg*4	0.99	2.67	3.544 (3)	147
C7—H7*B*···*Cg*2	0.99	3.00	3.827 (4)	142
C11—H11···*Cg*4^{iii}	0.95	2.70	3.615 (3)	161

C40—H40*A*···*Cg*1	0.99	2.72	3.630 (4)	153
C42—H42···*Cg*2^{i}	0.95	2.88	3.653 (4)	139
C52—H52*A*···*Cg*1^{iv}	0.99	2.80	3.790 (5)	176

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