organic compounds

Self-inclusion structure of 5,11,17,23-tetrakis(azidomethyl)-25,26,27,28-tetrahydroxycalix[4]arene, and 5,11,17,23-tetra-*tert*-butyl-25,27-bis(chloroacetoxy)-26,28-bis(2-pyridyl-methoxy)calix[4]arene

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In the structures of the two title calix[4]arene derivatives, $C_{32}H_{28}N_{12}O_4$, (I), and $C_{60}H_{68}Cl_2N_2O_6$, (II), compound (I) adopts an open-cone conformation in which there are four intramolecular O—H⋯O hydrogen bonds, while compound (II) adopts a distorted chalice conformation where the two pendant pyridyl rings, one of which is disordered, are almost mutually perpendicular, with an interplanar angle of 79.2 (2) or 71.4 (2)°. The dihedral angles between the virtual plane defined by the four bridging methylene C atoms and the phenol rings are 120.27 (7), 124.03 (6), 120.14 (8) and 128.25 (7)° for (I), and 95.99 (8), 135.93 (7), 97.21 (8) and 126.10 (8)° for (II). In the supramolecular structure of (I), pairs of molecules associate by self-inclusion, where one azide group of the molecule is inserted into the cavity of the inversion-related molecule, and the association is stabilized by weak intermolecular C—H⋯N hydrogen bonds and $\pi(N_3)$–π(aromatic) interactions. The molecular pairs are linked into a two-dimensional network by a combination of weak intermolecular C—H⋯N contacts. Each network is further connected to its neighbor to produce a three-dimensional framework *via* intersheet C—H⋯N hydrogen bonds. In the crystal packing of (II), the molecular components are linked into an infinite chain by intermolecular C—H⋯O hydrogen bonds. This study demonstrates the ability of calix[4]arene derivatives to form self-inclusion structures.

Comment

Calix[4]arenes, as the most fascinating macrocyclic receptors in supramolecular chemistry, have attracted much interest owing to their specific affinity and selectivity for ion recognition (Gutsche, 1998; Ungaro & Pochini, 1991; Böhmer, 1995).

This can be attained by appropriate chemical modifications to the upper or/and lower rims of a calix[4]arene platform (Gutsche, 1998), especially by incorporating organic functional groups containing N, O, P, S, Cl, *etc.* heteroatoms as donor centers. On the other hand, these molecules are useful building blocks for the construction of larger supramolecular assemblies. The crystal structures of self-inclusion aggregations based on some calix[4]arene derivatives have been described (Gallagher *et al.*, 1994; Böhmer *et al.*, 1996; Brouwer *et al.*, 2001; Ben Othman *et al.*, 2004). Recently, azide groups have been introduced successfully into the calix[4]arene platform in order to construct more sophisticated receptors *via* click chemistry (Rostovtsev *et al.*, 2002; Bew *et al.*, 2007; Colasson *et al.*, 2007; Vecchi *et al.*, 2008; Morales-Sanfrutos *et al.*, 2008); however, to the best of our knowledge, no examples of self-inclusion structures of such derivatives in the solid state have been described. We report here the self-inclusion structure of a calix[4]arene azide derivative, (I), as well as the structure of a *p-tert*-butylcalix[4]arene picolyl derivative, (II), namely 5,11,17,23-tetrakis(azidomethyl)-25,26,27,28-tetrahydroxycalix[4]arene and 5,11,17,23-tetra-*tert*-butyl-25,27-bis(chloroacetoxy)-26,28-bis(2-pyridylmethoxy)calix[4]arene, respectively.
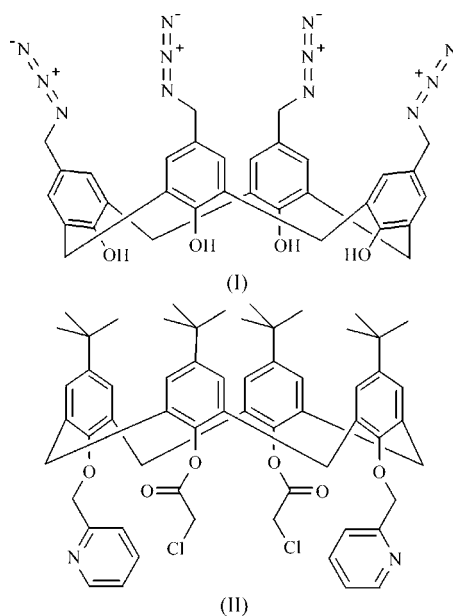
The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. Structural analysis reveals that (I) bears four –CH₂N₃ arms at the upper rim of the calix[4]arene platform, while about 9% of (I) has been converted into its analog in which one –CH₂N₃ unit has been oxidized into a –CHO group (Abbenante *et al.*, 2007), consistent with the results of MS analysis using the same crystals. We presume that the oxidation occurs during crystal growth or/and diffraction analysis on the basis of the fact that pure (I) was used when the crystallization was set up. Evaluation of the mechanism of this interesting event is currently in progress.

Compound (I) adopts an open-cone conformation, where an eight-membered ring is formed by intramolecular O—H⋯O hydrogen bonds connecting all four phenol hydroxy

groups, with O⋯O distances in the range 2.687 (3)–2.726 (3) Å (Table 1), and the four –CH$_2$N$_3$ arms are pitched slightly away from the calix cavity. Similar O⋯O distances [2.673 (2)–2.708 (2) Å] are observed in the structure of 5,17-diethoxycarbonyl-25,26,27,28-tetrahydroxycalix[4]arene (Böhmer *et al.*, 1996). The conformation in (I) leads to distances between diametrically opposed atoms O1 and O3, and O2 and O4 of 3.944 (3) and 3.683 (3) Å, respectively. The dihedral angles between the virtual plane (*R*) defined by the four bridging methylene C atoms and the C2–C7, C9–C14, C17–C22 and C25–C30 rings are 120.27 (7), 124.03 (6), 120.14 (8) and 128.25 (7)°, respectively.
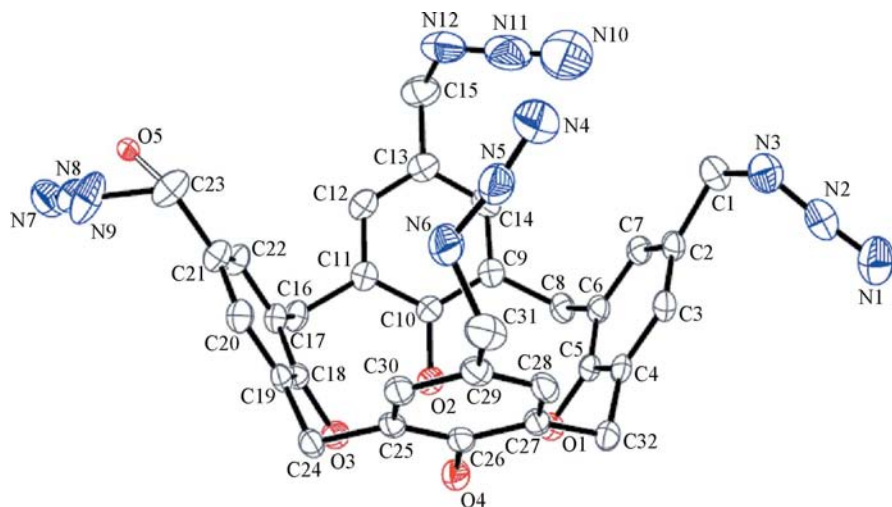

Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. The minor oxidized component is shown, but H atoms have been omitted for clarity.
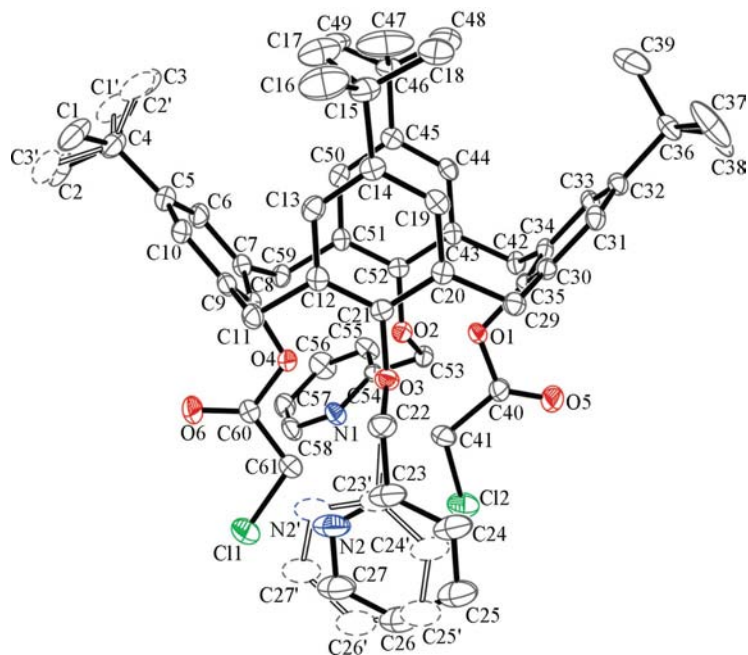

Figure 2
The molecular structure of (II), with displacement ellipsoids drawn at the 30% probability level. The minor disordered conformation has been included, but H atoms have been omitted for clarity.

Compound (II), which possesses two ClCH$_2$C(O)O– groups and two 2-pyridylmethoxy units at the lower rim of the *p-tert*-butylcalix[4]arene scaffold, has a distorted chalice conformation. One *tert*-butyl group shows rotational disorder, and one pyridyl ring is disordered over two orientations. The two pendant pyridyl rings are nearly perpendicular to one another, with interplanar angles of 79.2 (2) and 71.4 (2)° for the two disordered conformations, oriented in a fashion similar to that found in the structures of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(2-pyridylmethoxy)calix[4]arene (Pappalardo *et al.*, 1992) and l,3-bis(2-pyridylmethoxy)-*p-tert*-butylcalix[4]crown-5 (Gattuso *et al.*, 2006). The two opposing phenol rings bearing a ClCH$_2$C(O)O– group are tilted away from one another at an interplanar angle of 82.04 (9)° and make dihedral angles of 126.10 (8) and 135.93 (7)° with plane *R*, so that their *tert*-butyl groups are pitched away from the calix cavity. However, the other two phenol rings bearing a 2-pyridylmethoxy group are almost parallel to one another, with an interplanar angle of 13.21 (16)°, and create dihedral angles of 95.99 (8) and 97.21 (8)° with plane *R*. This conformation results in a separation between diametrically opposed atoms O1 and O4 of 3.996 (3) Å, which is much shorter than the distance of 4.987 (3) Å between atoms O2 and O3. Other molecular dimensions of both compounds are normal.

In the supramolecular structure of (I), novel self-inclusion occurs when the molecules pack in pairs about inversion centers, creating a loosely interlocked dimer (Fig. 3), in which one –CH$_2$N$_3$ arm of the molecule slots into the cavity of the inversion-related molecule. In each dimer, two weak intermolecular C—H⋯N hydrogen bonds (Table 1) locally form an $R_2^2(22)$ ring motif (Bernstein *et al.*, 1995) from atoms C20—H20 in the molecules at (*x, y, z*) and (−*x* + 1, −*y* + 1, −*z* + 2), which act as hydrogen-bond donors, to atoms N12 at (−*x* + 1, −*y* + 1, −*z* + 2) and (*x, y, z*), respectively. Moreover, an intermolecular π–π interaction was observed, with a $Cg1\cdots Cg2^i$ distance of 3.5409 (4) Å [*Cg*1 and *Cg*2 are the centroids of the C2–C7 ring and the N7–N9 group, respectively; symmetry code: (i) −*x* + 1, −*y* + 1, −*z* + 2]; the perpendicular distance between $Cg2^i$ and the plane of the C2–C7 ring is 3.1308 (3) Å. In this interaction, the N7–N9 group lies approximately parallel to the plane of the C2–C7 ring and close to
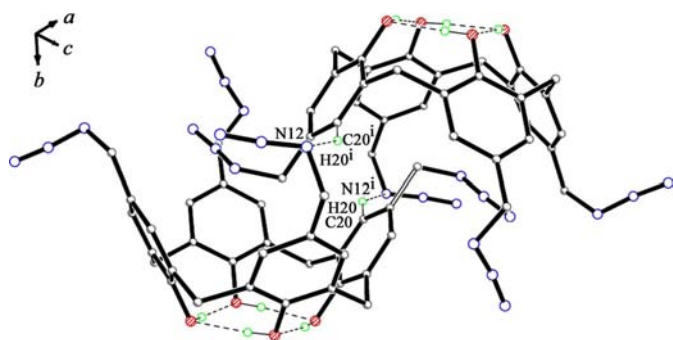
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Figure 3
A view of two inversion-related molecules of (I), showing the mutual inclusion with an $R_2^2(22)$ motif. For the sake of clarity, the minor oxidized component and H atoms not involved in the hydrogen bonds have been omitted. [Symmetry code: (i) $-x + 1, -y + 1, -z + 2$.]

atoms C2, C3 and C7. There have been several previous reports on the self-inclusion of calixarenes in the solid state (Gallagher *et al.*, 1994; Böhmer *et al.*, 1996; Brouwer *et al.*, 2001; Ben Othman *et al.*, 2004); however, this self-inclusion usually involves weak intermolecular C—H⋯π contacts. The structure of (I) is the first example of calixarene self-inclusion stabilized by weak intermolecular C—H⋯N hydrogen bonds and π(N₃)–π(aromatic) interactions. One azide group (N7–N9) of the molecule of (I) is anchored into the bowl-shaped cavity of an adjacent inversion-related molecule, while the others lie outside the calix bowl of the inversion-related molecule. Each dimer is linked to its neighbors to produce a two-dimensional network parallel to the *c* axis (Fig. 4) by a combination of intermolecular C32—H32A⋯N4($-x$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$) hydrogen bonds, locally forming a *C*(9) chain motif
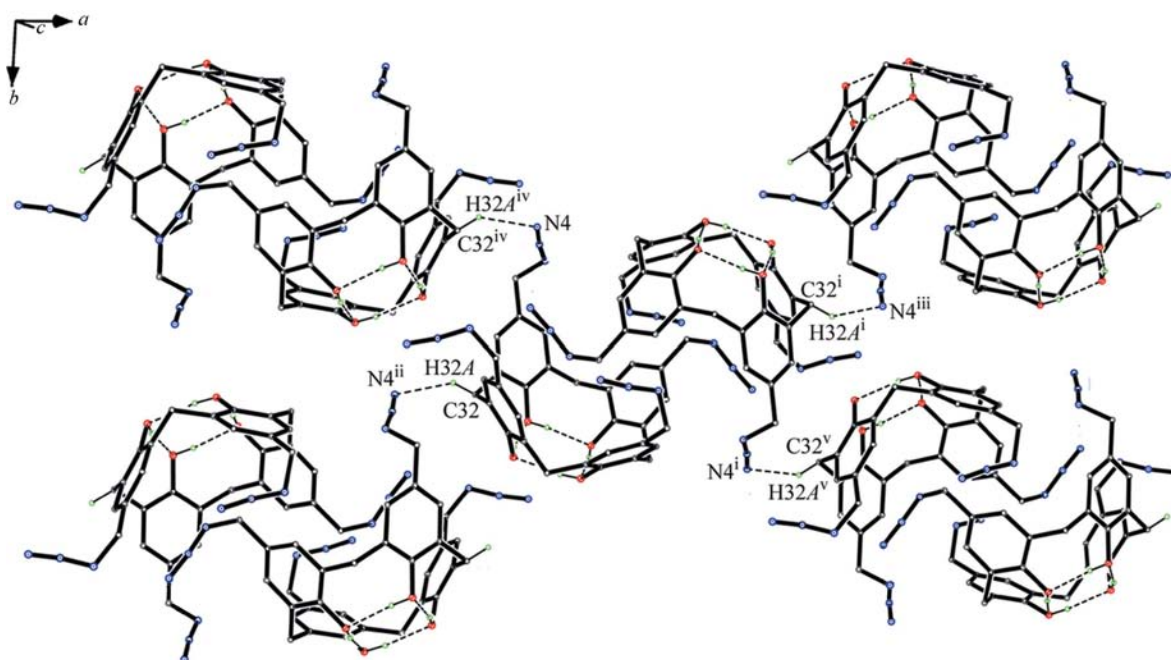

Figure 4
The two-dimensional network of (I), viewed along the *c* axis, showing the *C*(9) motifs. For the sake of clarity, the minor oxidized component and H atoms not involved in the motifs shown have been omitted. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 2$; (ii) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; (v) $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$.]
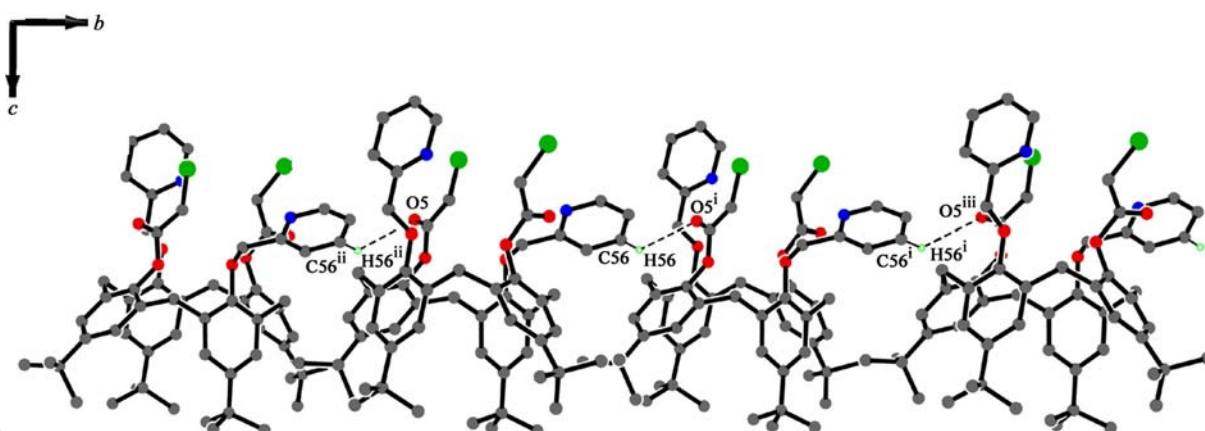

Figure 5
The hydrogen-bonded one-dimensional chain of (II), viewed along the *a* axis, showing the *C*(14) motifs along [010]. For the sake of clarity, the minor disordered atoms and H atoms not involved in the motifs shown have been omitted. [Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, z$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (iii) $x, y + 1, z$.]

(Bernstein *et al.*, 1995) at each link in the network. Neighboring networks are further connected to a three-dimensional framework *via* intersheet C15—H15*A*···N7(x, $-y + \frac{3}{2}$, $z - \frac{1}{2}$) interactions, locally creating a $C(13)$ chain motif (Bernstein *et al.*, 1995).

In the crystal structure of (II), there are several intra- and intermolecular C—H···O and C—H···N short contacts (Table 2), although no classical hydrogen bonds are found. The intramolecular C41—H41*A*···O2, C41—H41*B*···O3 and C42—H42*A*···O5 interactions result in atoms O1, C40, C41 and Cl2 of one ClCH₂C(O)O– group approaching plane R more closely than the equivalent atoms of the other ClCH₂C(O)O– group. A hydrogen-bonded infinite chain parallel to [010] (Fig. 5) is formed by a combination of intermolecular C56—H56···O5($-x + \frac{3}{2}$, $y + \frac{1}{2}$, z) interactions, which locally creates a $C(14)$ motif (Bernstein *et al.*, 1995) at each link in the chain.

Experimental

For the synthesis of (I), a solution of *p*-chloromethylcalix[4]arene (0.300 g, 0.49 mmol), prepared according to a published procedure (Kotch *et al.*, 2003), and NaN₃ (0.319 g, 4.90 mmol) in dimethylformamide (10 ml) was stirred at 343 K for 8 h. After removal of the solvent under reduced pressure, the residue was extracted with CH₂Cl₂ and washed with brine. The organic layer was dried over anhydrous MgSO₄. Removal of the solvent gave (I) as a white solid (yield 85%; m.p. 423 K, decomposition), which was purified by recrystallization from CH₃OH/CH₂Cl₂. ¹H NMR (300 MHz, CDCl₃): δ 10.12 (*s*, 4H), 7.02 (*s*, 8H), 4.26 (*d*, 4H, J = 12.5 Hz), 4.15 (*s*, 8H), 3.58 (*d*, 4H, J = 12.6 Hz). MS (analyzed using the crystals) *m/e*: 667.5 ([*M* + Na]⁺), 645.6 ([*M* + 1]⁺), 640.7 ([*M′* + Na]⁺), 618.7 ([*M′* + 1]⁺).

For the synthesis of (II), chloroacetyl chloride (0.19 ml, 2.4 mmol) was added dropwise to a stirred suspension of 5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-pyridylmethoxy)-26,28-dihydroxycalix[4]arene (0.200 g, 0.24 mmol), obtained according to a published procedure (Pappalardo *et al.*, 1992), and NaH (0.029 g, 80%, 0.96 mmol) in dry tetrahydrofuran (15 ml) at 273 K. The resulting mixture was stirred for 20 h at 343 K. After removal of the solvent under reduced pressure, the residue was poured into an ice–water mixture, extracted with CH₂Cl₂ and washed with brine. The organic layer was dried over anhydrous MgSO₄. Removal of the solvent gave (II) as a white solid (yield 74%; m.p. 492 K, decomposition), which was purified by flash column chromatography (EtOAc/hexane = 1:4, R_F = 0.4). ¹H NMR (300 MHz, CDCl₃): δ 8.80 (*d*, 2H, J = 4.0 Hz), 7.78 (*t*, 2H, J = 7.6 Hz), 7.36 (*s*, 2H), 7.33 (*s*, 2H), 7.24 (*s*, 4H), 6.71 (*s*, 4H), 4.76 (*s*, 4H), 4.71 (*s*, 4H), 4.14 (*d*, 4H, J = 12.9 Hz), 3.27 (*d*, 4H, J = 12.9 Hz), 1.36 (*s*, 18H), 0.89 (*s*, 18H). Single crystals of (I) and (II) suitable for X-ray diffraction analysis were obtained by slow evaporation of solutions in CH₃OH and CH₂Cl₂, respectively, at 273 K.

Compound (I)

Crystal data

C₃₂H₂₇.₉₁N₁₁.₇₃O₄.₀₉	V = 2975.3 (9) Å³
M_r = 642.20	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 12.377 (2) Å	μ = 0.10 mm⁻¹
b = 12.446 (2) Å	T = 298 K
c = 19.979 (3) Å	0.38 × 0.28 × 0.16 mm
β = 104.812 (3)°	

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O2	0.82	1.88	2.695 (3)	172
O4—H4···O3	0.82	1.88	2.687 (3)	170
O1—H1···O4	0.82	1.88	2.690 (3)	167
O2—H2···O1	0.82	1.92	2.726 (3)	169
C20—H20···N12ⁱ	0.93	2.66	3.472 (4)	146
C15—H15A···N7ᵛⁱ	0.97	2.43	3.346 (5)	157
C32—H32A···N4ⁱⁱ	0.97	2.64	3.386 (5)	134

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

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

D—H···A	D—H	H···A	D···A	D—H···A
C41—H41A···O2	0.99	2.36	3.1214 (14)	133
C41—H41B···O3	0.99	2.52	3.2783 (15)	133
C42—H42A···O5	0.99	2.60	3.2842 (15)	127
C61—H61B···N1	0.99	2.49	3.4007 (17)	152
C56—H56···O5ⁱ	0.95	2.56	3.2406 (17)	129

Symmetry code: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, z$.

Data collection

Bruker SMART CCD area-detector diffractometer	5228 independent reflections
	3717 reflections with $I > 2\sigma(I)$
14693 measured reflections	R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060	447 parameters
$wR(F^2)$ = 0.168	H-atom parameters constrained
S = 1.03	$\Delta\rho_{max}$ = 0.36 e Å⁻³
5228 reflections	$\Delta\rho_{min}$ = −0.23 e Å⁻³

Compound (II)

Crystal data

C₆₀H₆₈Cl₂N₂O₆	V = 11394 (3) Å³
M_r = 984.06	Z = 8
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
a = 19.280 (3) Å	μ = 0.16 mm⁻¹
b = 21.358 (4) Å	T = 173 K
c = 27.670 (5) Å	0.45 × 0.21 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer	57503 measured reflections
	10602 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	6355 reflections with $I > 2\sigma(I)$
T_{min} = 0.930, T_{max} = 0.976	R_{int} = 0.082

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065	219 restraints
$wR(F^2)$ = 0.192	H-atom parameters constrained
S = 1.02	$\Delta\rho_{max}$ = 0.65 e Å⁻³
10602 reflections	$\Delta\rho_{min}$ = −0.39 e Å⁻³
729 parameters	

All H atoms were placed in geometrically idealized positions and refined using a riding model, with C—H distances of 0.93–0.99 Å, and with U_{iso}(H) values of $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(C) for all other H atoms. In (I), one N₃ group is disordered with the O

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atom of an aldehyde decomposition product. The site-occupation factors of the disordered atoms refined to 0.909 (5) for atoms N7–N9 and 0.091 (5) for atom O5. In (II), one *tert*-butyl group (C1–C4) shows rotational disorder; the site-occupation factor of the major orientation (C1, C2 and C3) is 0.5554 (13). The C—C bond lengths involving the disordered atoms were restrained to be similar, and the refined distances lie in the range 1.507 (3)–1.582 (3) Å. One pyridyl ring in (II) (C23–C27/N2) is also disordered over two positions; the site-occupancy factor of the major conformation defined by atoms C23–C27/N2 refined to 0.5165 (13). The C—C and C—N bonds involving the disordered atoms were restrained to be similar, and the refined distances lie in the ranges 1.363 (4)–1.482 (4) and 1.335 (3)–1.407 (4) Å, respectively, while the atomic displacement parameters of adjacent atoms in both conformations of the disordered ring were restrained to be similar.

For both compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3123). Services for accessing these data are described at the back of the journal.

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