

1:1 Adducts of 2,2'-[isopropylidenebis(*p*-phenyleneoxy)]diacetic acid with dimethylammonium and 4,4'-bipyridine

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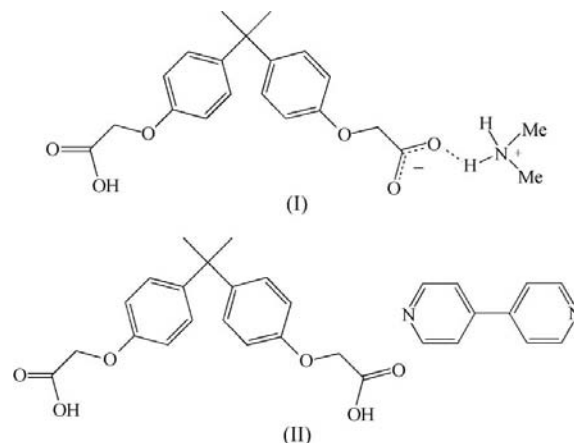
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The title compounds, dimethylammonium 2-[4-[1-(4-carboxymethoxyphenyl)-1-methylethyl]phenoxy]acetate, $C_{21}H_{27}N^+ \cdot C_{19}H_{19}O_6^-$, (I), and 2,2'-[isopropylidenebis(*p*-phenyleneoxy)]diacetic acid–4,4'-bipyridine (1/1), $C_{19}H_{20}O_6 \cdot C_{10}H_8N_2$, (II), are 1:1 adducts of 2,2'-[isopropylidenebis(*p*-phenyleneoxy)]diacetic acid (H_2L) with dimethylammonium or 4,4'-bipyridine. The component ions in (I) are linked by N—H···O, O—H···O and C—H···O hydrogen bonds into continuous two-dimensional layers parallel to the (001) plane. Adjacent layers are stacked *via* C—H···O hydrogen bonds into a three-dimensional network with an *–ABAB–* alternation of the two-dimensional layers. In (II), two H_2L molecules, one bipy molecule and two half bipy molecules are linked by O—H···N hydrogen bonds into one-dimensional chains and rectangular-shaped rings. They are assembled *via* π – π stacking interactions and C—H···O hydrogen bonds into an intriguing zero-dimensional plus one-dimensional poly(pseudo)rotaxane motif.

Comment

Over the past decade, the rational design and synthesis of metal–organic frameworks have received extensive attention in the fields of supramolecular chemistry and crystal engineering (Rosi *et al.*, 2003; Dalgarno *et al.*, 2008). These materials exhibit interesting properties, such as catalysis, biological activity, electrical conductivity, magnetism and photochemical activity. In the past five years, there has been a growing interest in metal–organic frameworks involving semi-rigid V-shaped dicarboxylate ligands (Tanaka *et al.*, 2008; Zang *et al.*, 2006; Mahata *et al.*, 2008; Furukawa *et al.*, 2008). 2,2'-[Isopropylidenebis(*p*-phenyleneoxy)]diacetic acid (H_2L) is a typical example of a semi-rigid V-shaped dicarboxylate ligand. To the best of our knowledge, there has been no report to date concerning its coordination compounds. Recently, we have

focused on preparing metal–organic frameworks containing this organic ligand and metal ions. During this process, two interesting adducts of H_2L with dimethylammonium and 4,4'-bipyridine, (I) and (II), respectively, were obtained, and we report here their synthesis and crystal structures.



Although we failed to formulate coordination polymers at this stage, the present characterization of the crystalline products provides useful information. Thus, when H_2L was reacted with a lanthanum nitrate salt (see *Experimental*) in the presence of *N,N*-dimethylformamide (DMF) under hydrothermal conditions, no metal ions were incorporated into the structure. Instead, the 1:1 salt, (I), formed between the monodeprotonated H_2L and a dimethylammonium cation (a product resulting from hydrolysis of DMF). The H atom of one carboxyl group is transferred to the dimethylamine N atom, while the other remains as the acid. The carboxyl and carboxylate groups are almost perpendicular to the benzene ring, with dihedral angles of 80.9 (1) and 86.2 (2)°, respectively (Table 1 and Fig. 1). The arrangement in the carboxylic acid is the less common *syn-anti* conformation (Kennard *et al.*, 1982; Lynch *et al.*, 2003). The benzene rings of the bent HL anion subtend a dihedral angle of 86.5 (1)°.

The supramolecular structure of (I) can be simply analyzed in terms of three substructures. Firstly, the HL^- anions result in discrete one-dimensional chains *via* an O5—H5···O2A hydrogen bond [symmetry code: (A) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$] running parallel to the [010] direction. Secondly, adjacent

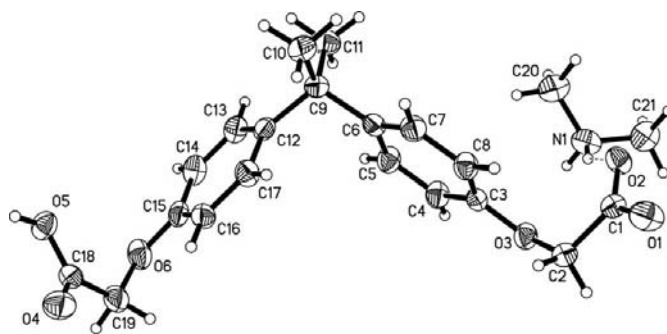
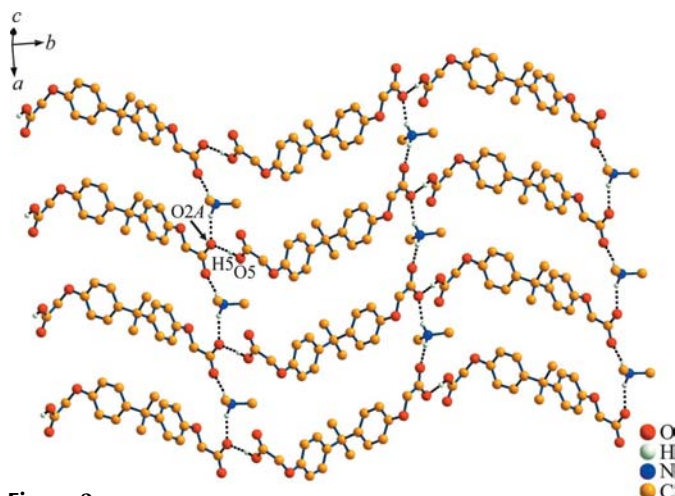


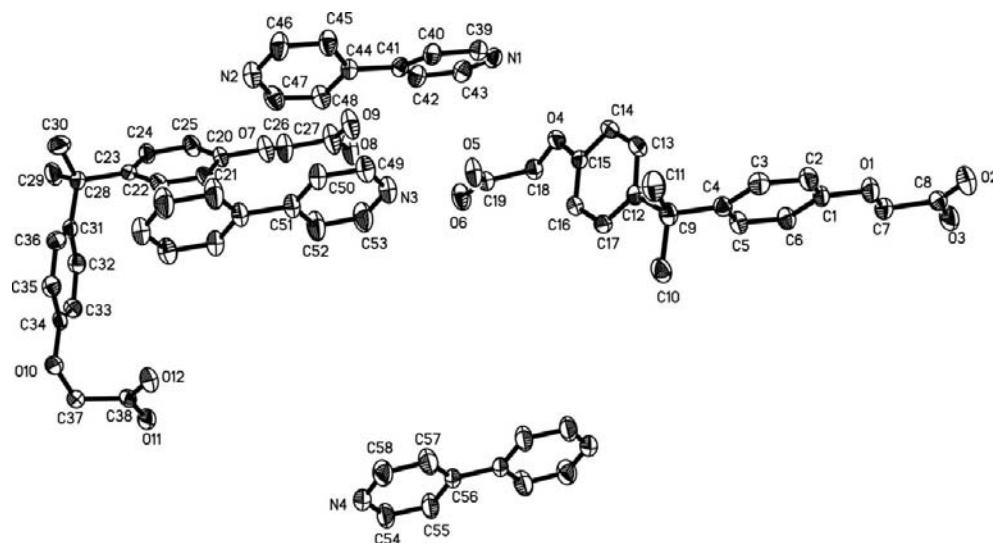
Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.


Figure 2

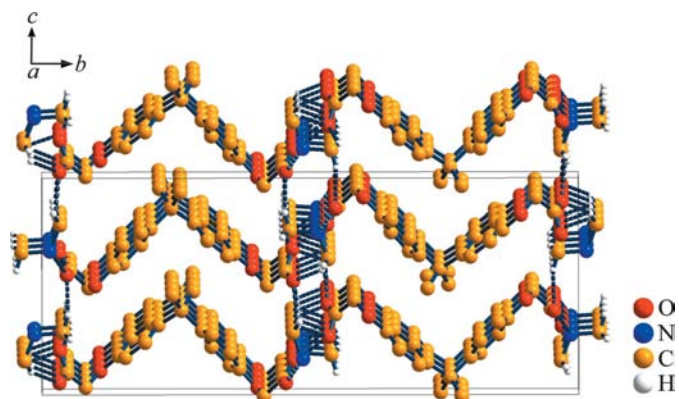
Part of the crystal structure of (I), showing the formation of the two-dimensional layer running parallel to the (001) plane. Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms not involved in the motif have been omitted. [Symmetry code: (A) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$.]

[010] chains are linked together by dimethylammonium cations through strong N—H···O hydrogen bonds in concert with C—H···O hydrogen bonds (Table 2), forming two-dimensional layers built from $R_4^6(46)$ hydrogen-bond motifs (Bernstein *et al.*, 1995) which are parallel to the (001) plane (Fig. 2). Finally, neighbouring two-dimensional layers are assembled into a three-dimensional network by means of C—H···O hydrogen bonds with an $-ABAB-$ alternation of the two-dimensional layers (Fig. 3 and Table 2).

The reaction of H_2L with Pb^{II} ions in the presence of 4,4'-bipyridyl (bipy) yielded compound (II). As shown in Fig. 4, the asymmetric unit of (II) consists of two H_2L molecules and one bipy molecule, together with two half-bipy molecules, these last both possessing inversion centres. The C—O bond distances support the existence of un-ionized acid molecules, indicating cocrystal formation (Table 3). H_2L and bipy crys-


Figure 4

The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.


Figure 3

The extended structure of the three-dimensional supramolecular network of (I), viewed along the a axis. H atoms not involved in hydrogen bonding have been omitted for clarity.

tallize to form two different independent networks, a four-membered rectangular-shaped ring (Fig. 5a) and a one-dimensional wave-like chain (Fig. 5b). In both networks, the H_2L and bipy molecules are linked together by strong O—H···N hydrogen bonds (Table 4). In the rectangular-shaped ring, the planes of the pyridyl rings of the bipy molecule are twisted by $25.9(6)^\circ$ with respect to each other. One of the phenoxyacetic acid groups (containing atom O11) adopts an antiperiplanar conformation, with a dihedral angle of $44.3(2)^\circ$ between the carboxyl group and the benzene ring. The other phenoxyacetic acid group (containing atom O8) adopts a synplanar conformation, with a dihedral angle of $82.2(1)^\circ$. The dihedral angle between the two benzene rings is $88.2(2)^\circ$. In the chain network, the bipy molecules, which lie on centres of inversion, both have planar central portions. The conformation of the H_2L molecule shows some differences from the H_2L molecule in the rectangular ring. One phenoxyacetic acid group (containing atom O3) has an antiperiplanar conformation and the acetic acid arm is almost in the same plane as the

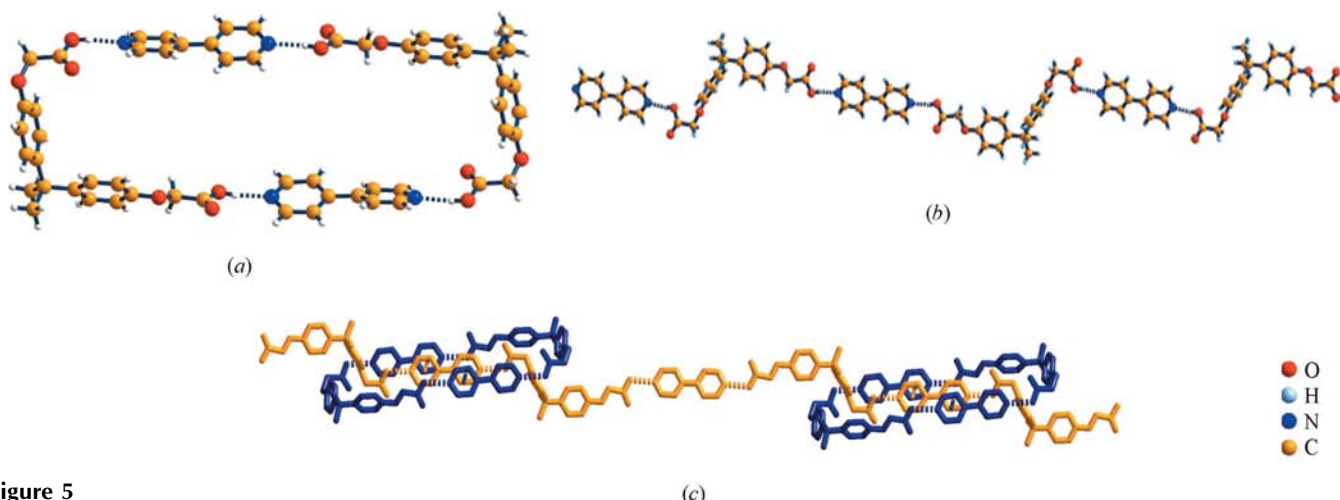


Figure 5
 (a) The rectangular-shaped ring formed by the intermolecular $O11-H11 \cdots N1(-x+1, -y+1, -z+1)$ and $O8-H8 \cdots N2(x-1, y, z)$ hydrogen bonds in (II). (b) The one-dimensional chain formed by the $O3-H3 \cdots N4(x-1, y, z-1)$ and $O5-H5 \cdots N3$ hydrogen bonds in (II). H atoms not involved in the interactions have been omitted for clarity. (c) The zero-dimensional plus one-dimensional poly(pseudo)rotaxane motif in (II). H atoms have been omitted for clarity.

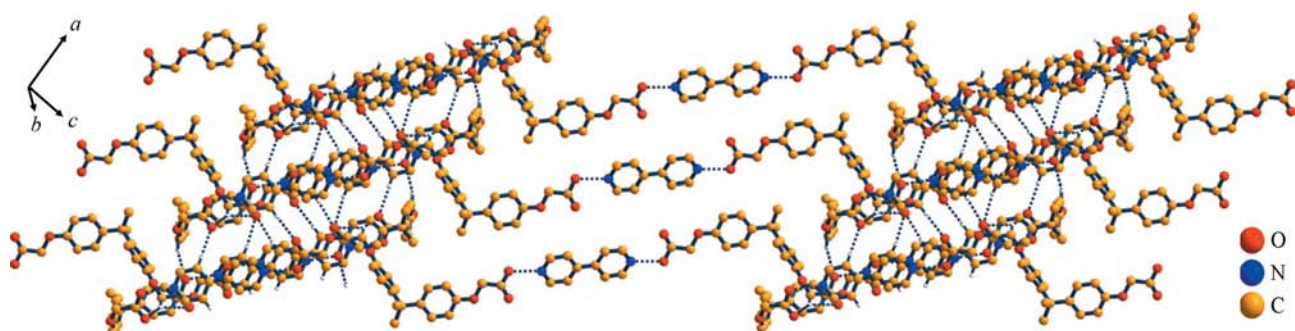


Figure 6
 The extended supramolecular hydrogen-bonded network of (II). H atoms not involved in hydrogen bonding have been omitted for clarity.

benzene ring. The other phenoxyacetic acid group adopts an uncommon *syn-anti* conformation, like that in (I), and here the dihedral angle between the two benzene rings is $85.9(2)^\circ$.

Interestingly, the rectangular rings and wave-like chains are assembled by π - π stacking interactions and $C18-H18B \cdots O12(-x+1, -y+1, -z+1)$ hydrogen bonds into an intriguing zero-dimensional plus one-dimensional poly(pseudo)rotaxane motif (Fig. 5c). The π - π interactions occur between the bipy rings containing atoms N2 and N3, with a ring centroid distance of $3.874(3)$ Å, an interplanar spacing of $3.541(2)$ Å and an offset angle of $4.20(1)^\circ$. The poly(pseudo)rotaxane motifs are linked into a three-dimensional network by a combination of $C-H \cdots O$ and $C-H \cdots \pi$ hydrogen bonds (Table 4 and Fig. 6).

In conclusion, the two 1:1 organic compounds formed by H_2L with dimethylammonium and bipy are the first examples of H_2L adducts to be described. The phenoxyacetic acid groups in these two adducts show interesting conformations, and an intriguing zero-dimensional plus one-dimensional poly(pseudo)rotaxane structure is found in compound (II) (Fig. 5c).

Experimental

H_2L was synthesized according to the literature method of Inouye *et al.* (1995). Compound (I) was obtained by heating a mixture of $La(NO_3)_3 \cdot 6H_2O$ (0.130 g, 0.3 mmol), H_2L (0.206 g, 0.6 mmol) and DMF (3 ml) in a sealed 5 ml reactor at 433 K for 48 h, followed by gradual cooling to room temperature. Colourless block-shaped crystals of (I) were collected by filtration and air-dried. Compound (II) was obtained when a mixture of $Pb(NO_3)_2$ (0.109 g, 0.33 mmol), bipy (0.019 g, 0.12 mmol) and H_2L (0.042 mg, 0.12 mmol) in H_2O (8 ml) was sealed in a 25 ml Teflon-lined stainless steel reactor and heated at 443 K for 72 h. A crop of colourless single platelet-shaped crystals was obtained after cooling the solution to room temperature and these were collected and washed with distilled water.

Compound (I)

Crystal data

$C_{28}H_{38}N^+ \cdot C_{19}H_{19}O_6^-$
 $M_r = 389.44$
 Monoclinic, $P2_1/c$
 $a = 6.9028(14)$ Å
 $b = 27.756(6)$ Å
 $c = 12.624(4)$ Å
 $\beta = 120.21(2)^\circ$

$V = 2090.2(9)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 295$ K
 $0.20 \times 0.18 \times 0.17$ mm

Table 1

Selected geometric parameters (Å, °) for (I).

| | | | |
|-------------|------------|----------------|------------|
| O1—C1 | 1.231 (3) | O4—C18 | 1.196 (3) |
| O2—C1 | 1.258 (3) | O5—C18 | 1.308 (3) |
| C3—O3—C2—C1 | −80.7 (2) | C19—O6—C15—C14 | −173.4 (2) |
| O1—C1—C2—O3 | 170.0 (2) | C15—O6—C19—C18 | 69.4 (3) |
| C2—O3—C3—C4 | −166.7 (2) | O5—C18—C19—O6 | 25.0 (3) |

Table 2

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

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| O5—H5...O2 ⁱ | 0.82 | 1.70 | 2.507 (2) | 167 |
| N1—H1B...O1 ⁱⁱⁱ | 0.90 | 1.87 | 2.758 (3) | 169 |
| N1—H1A...O3 | 0.90 | 2.54 | 3.245 (3) | 136 |
| N1—H1A...O2 | 0.90 | 1.98 | 2.800 (3) | 151 |
| C20—H20A...O4 ⁱⁱⁱ | 0.96 | 2.47 | 3.368 (4) | 155 |
| C20—H20C...O4 ^{iv} | 0.96 | 2.58 | 3.300 (4) | 132 |
| C20—H20C...O5 ^v | 0.96 | 2.58 | 3.374 (3) | 140 |
| C21—H21A...O5 ^v | 0.96 | 2.45 | 3.282 (3) | 145 |
| C21—H21B...O1 ^{vi} | 0.96 | 2.54 | 3.390 (4) | 148 |

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

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.982, T_{\max} = 0.985$
 10877 measured reflections
 3693 independent reflections
 2126 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.134$
 $S = 1.03$
 3693 reflections
 257 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.12 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.17 \text{ e } \text{Å}^{-3}$

Compound (II)

Crystal data

$\text{C}_{19}\text{H}_{20}\text{O}_6 \cdot \text{C}_{10}\text{H}_8\text{N}_2$
 $M_r = 500.53$
 Triclinic, $P\bar{1}$
 $a = 8.8698 (15) \text{ Å}$
 $b = 14.673 (2) \text{ Å}$
 $c = 20.087 (3) \text{ Å}$
 $\alpha = 96.749 (2)^\circ$
 $\beta = 94.180 (3)^\circ$
 $\gamma = 99.751 (4)^\circ$
 $V = 2547.1 (7) \text{ Å}^3$
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.09 \text{ mm}^{-1}$
 $T = 295 \text{ K}$
 $0.22 \times 0.18 \times 0.16 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.980, T_{\max} = 0.985$
 13525 measured reflections
 8949 independent reflections
 4313 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.070$
 $wR(F^2) = 0.235$
 $S = 1.02$
 8949 reflections
 670 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.74 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.41 \text{ e } \text{Å}^{-3}$

Table 3

Selected geometric parameters (Å, °) for (II).

| | | | |
|----------------|------------|-----------------|------------|
| O2—C8 | 1.201 (5) | O8—C27 | 1.291 (6) |
| O3—C8 | 1.306 (6) | O9—C27 | 1.169 (5) |
| O5—C19 | 1.289 (5) | O11—C38 | 1.316 (5) |
| O6—C19 | 1.211 (5) | O12—C38 | 1.218 (5) |
| C7—O1—C1—C2 | 177.3 (4) | C26—O7—C20—C21 | 152.7 (5) |
| C1—O1—C7—C8 | −177.3 (3) | C20—O7—C26—C27 | −179.6 (4) |
| O1—C7—C8—O3 | 179.2 (4) | O7—C26—C27—O8 | 164.1 (5) |
| C18—O4—C15—C14 | 167.5 (4) | C37—O10—C34—C35 | −160.6 (3) |
| C15—O4—C18—C19 | 86.2 (4) | C34—O10—C37—C38 | 69.6 (4) |
| O4—C18—C19—O5 | −14.5 (5) | O10—C37—C38—O11 | −161.5 (3) |

Table 4

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

*Cg*1 and *Cg*2 are the centroids of the C20–C25 and C12–C17 rings, respectively.

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|---------------------------------------|-------------|---------------|-----------------------|-------------------------|
| O3—H3...N4 ⁱ | 0.82 | 1.78 | 2.584 (5) | 166 |
| O5—H5...N3 | 0.82 | 1.75 | 2.561 (5) | 169 |
| O8—H8...N2 ⁱⁱ | 0.82 | 1.84 | 2.647 (5) | 166 |
| O11—H11...N1 ⁱⁱⁱ | 0.82 | 1.84 | 2.647 (4) | 167 |
| C18—H18B...O12 ⁱⁱⁱ | 0.97 | 2.39 | 3.227 (5) | 144 |
| C35—H35...O5 ^{iv} | 0.93 | 2.54 | 3.245 (5) | 133 |
| C40—H40...O12 ^{iv} | 0.93 | 2.50 | 3.432 (5) | 176 |
| C42—H42...O9 | 0.93 | 2.56 | 3.476 (5) | 170 |
| C50—H50...O6 ^v | 0.93 | 2.56 | 3.458 (6) | 162 |
| C52—H52...O6 ⁱⁱⁱ | 0.93 | 2.52 | 3.414 (6) | 162 |
| C16—H16... <i>Cg</i> 1 ⁱⁱⁱ | 0.93 | 2.90 | 3.669 (5) | 141 |
| C32—H32... <i>Cg</i> 2 ⁱⁱⁱ | 0.93 | 2.89 | 3.625 (5) | 137 |

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

H atoms were located in difference maps, but were subsequently placed in calculated positions and treated as riding, with O—H = 0.82 Å, N—H = 0.90 Å and C—H = 0.93–0.97 Å, and refined as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C and N})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}} \text{ and O})$. For (II), the *R* factor is slightly higher than normally expected due to the fact that the crystal diffracted weakly, and only 48% of the data can be considered to be observed [$I > 2\sigma(I)$].

For both compounds, data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: PLATON (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3040). Services for accessing these data are described at the back of the journal.

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