

Two polymorphs of 2-(4-chlorophenyl)-4-methylchromenium perchlorate

Alexander D. Roshal,^a Artur Sikorski,^b Vyacheslav N. Baumer,^c Alexander I. Novikov^d and Jerzy Błażejowski^{b*}

^aInstitute of Chemistry, V. N. Karazin Kharkiv National University, Svoboda Square 4, 60177 Kharkiv, Ukraine, ^bFaculty of Chemistry, University of Gdańsk, J. Sobieskiego 18, 80-952 Gdańsk, Poland, ^cInstitute for Single Crystals, National Academy of Science of Ukraine, Lenin Avenue 60, 60001 Kharkiv, Ukraine, and ^dKharkiv Military University, Svoboda Square 6, 61022 Kharkiv, Ukraine
Correspondence e-mail: bla@chem.univ.gda.pl

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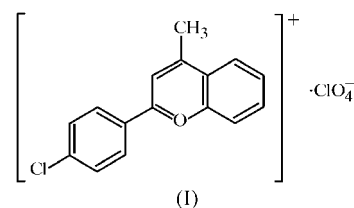
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Crystallization (from ethyl acetate solution) of 2-(4-chlorophenyl)-4-methylchromenium perchlorate, $C_{16}H_{12}ClO^+ \cdot ClO_4^-$, (I), yields two monoclinic polymorphs with the space groups $P2_1/n$ [polymorph (Ia)] and $P2_1/c$ [polymorph (Ib)]; in both cases, $Z = 4$. Cations and anions, disordered in polymorph (Ib), form ion pairs in both polymorphs as a result of $Cl-O \cdots \pi$ interactions. Related by a centre of symmetry, neighbouring ion pairs in polymorph (Ia) are linked *via* $\pi-\pi$ interactions between cationic fragments, and the resulting dimers are linked through a network of $C-H \cdots O$ (perchlorate) interactions between adjacent cations and anions. The ion pairs in polymorph (Ib), arranged in pairs of columns along the a axis, are linked through a network of $C-H \cdots O$ (perchlorate), $C-Cl \cdots \pi$, $\pi-\pi$ and $C-Cl \cdots O$ (perchlorate) interactions. The aromatic skeletons in polymorph (Ia) are parallel in the cationic fragments involved in dimers, but nonparallel in adjacent ion pairs not constituting dimers. In polymorph (Ib), these skeletons are parallel in pairs of columns, but nonparallel in adjacent pairs of columns; this is visible as a herring-bone pattern. Differences in the crystal structures of the polymorphs are most probably the cause of their different colours.

Comment

2-Phenylchromenium salt-type systems occur in natural dyes (anthocyanides), exhibiting a distinctive biological significance (Gera, 1982). Owing to their strong absorption in the orange-red spectroscopic region, they are used as dyes, for example, in the food industry (Timberlake & Bridle, 1980). Some 2-phenylchromenium salts exhibit intense luminescence and are used as lasing materials (Maeda, 1984; Deligeorgiev *et al.*, 1987). Our investigations of the features of 2-phenylchromenium cations and their dimers and nucleophilic

complexes (Roshal *et al.*, 1998; Roshal *et al.*, 2002) have shown that the spectroscopic properties of these species depend on their structure, mainly the angle between the chromium and phenyl fragments (Roshal, 1999). The opportunity of investigating the influence of structure on spectroscopic features arose when we found two polymorphs of different colours following the crystallization of 2-(4-chlorophenyl)-4-methylchromenium perchlorate from ethyl acetate, subsequently designated (Ia) and (Ib). There is, to our knowledge, only one report in the Cambridge Structural Database (Version 5.28; Allen, 2002) concerning 2-phenylchromenium derivatives (Busetta *et al.*, 1974). The present work thus extends our knowledge of the crystal structures of this important group of compounds.



The parameters characterizing the geometry of the aromatic skeleton in both polymorphs are given in Tables 1 and 5. The relevant bond lengths, as well as the valence and dihedral angles, are comparable, except for the $C3-C2-C11-C12$ angle, which differs by $2.0 (5)^\circ$. The angle between the mean planes of rings 1 (defined by atoms $O1/C2-C4/C9/C10$) and 2 (defined by atoms $C5-C8/C9/C10$) is $0.0 (2)^\circ$ in polymorph (Ia) and $1.5 (5)^\circ$ in polymorph (Ib). Furthermore, the angle between the mean planes of the chromenium skeleton (defined by atoms $O1/C2-C10$) and ring 3 (defined by atoms $C11-C16$) is $5.2 (2)^\circ$ in polymorph (Ia) and $1.6 (5)^\circ$ in polymorph (Ib). This implies that all three rings lie almost in one plane in both polymorphs.

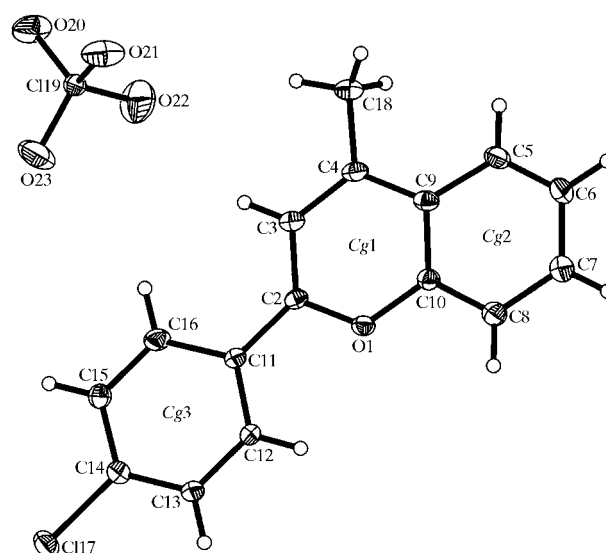


Figure 1
The molecular structure of polymorph (Ia), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radii. $Cg1-Cg3$ denote the ring centroids.

In polymorph (Ia) (Fig. 1), the cations and the anions form ion pairs *via* Cl–O··· π interactions (Fig. 2 and Table 3). Adjacent ion pairs, related by a centre of symmetry, are linked *via* π – π interactions between cationic fragments (involving rings 1 and 3) (Table 4), and the resulting dimers are linked through a network of C–H···O(perchlorate) interactions (Table 2) between the cationic and anionic fragments of

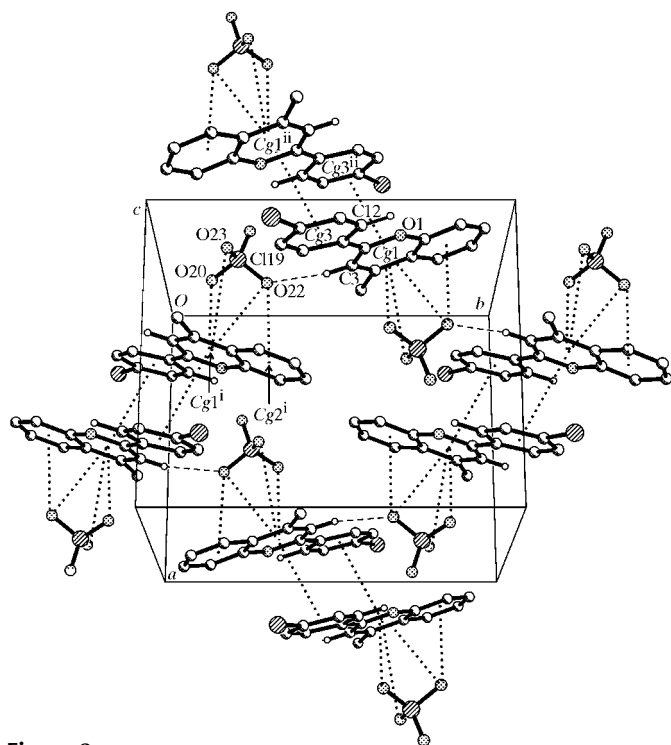


Figure 2

The arrangement of the ions of polymorph (Ia) in the unit cell, viewed approximately along the *c* axis. The C–H···O interactions are represented by dashed lines, and Cl–O··· π and π – π interactions by dotted lines. H atoms not involved in the interactions have been omitted. [Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $-x, 1 - y, 2 - z$.]

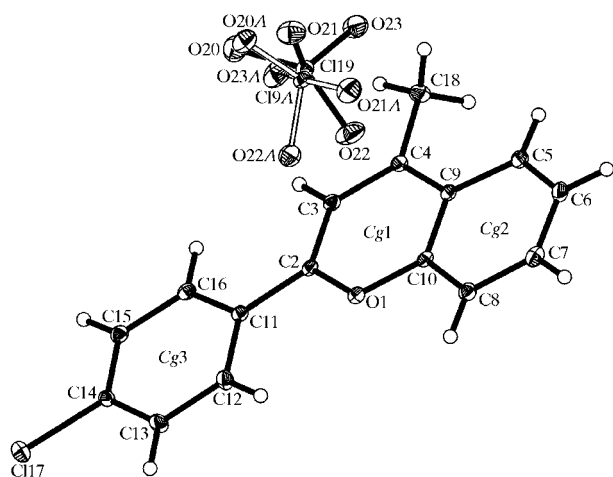


Figure 3

The molecular structure of polymorph (Ib), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radii. The minor disorder component of the perchlorate anion is drawn with open bonds.

neighbouring ion pairs (Fig. 2). The angle between the mean planes defined by the whole aromatic skeleton (defined by atoms O1/C2–C16) is either 0° , in the case of the cationic fragments involved in dimers, or $32.6(2)^\circ$, if we take into account the cationic fragments of adjacent ion pairs not constituting dimers.

The tetrahedral perchlorate anions in polymorph (Ib) occupy two positions, with occupancy factors of 0.557 (11) and 0.443 (11) for Cl19/O20–O23 and Cl9A/O20A–O23A, respectively (Fig. 3). Disordered perchlorate anions have been reported by others (*e.g.* Sun, 2005; Athimoolam & Rajaram, 2006), which suggests that disorder is not a feature unique to this entity. The assumed model, however, only partially describes the overall perchlorate disorder. The cations and anions form ion pairs *via* Cl–O··· π interactions (Figs. 4 and 5, and Table 7). The ion pairs are arranged in columns extending along the *a* axis, in which the aromatic skeletons are parallel to one another (Fig. 4) and inclined at an angle of $63.6(5)^\circ$ relative to the *bc* plane. Cations of neighbouring ion pairs in columns are linked *via* π – π interactions, whereas cations and anions do so *via* C–H···O (perchlorate) interactions (Fig. 4, and Tables 6 and 8). Adjacent columns are linked *via* C–Cl··· π and π – π interactions between cations (Fig. 5, and Tables 7 and 8), forming pairs of columns. Within a pair of columns, the aromatic skeletons are parallel. In adjacent pairs of columns, linked through C–H···O(perchlorate) interactions (Fig. 5 and Table 6) and O···Cl contacts [Cl17···O23–(1–*x*, *y*– $\frac{1}{2}$, $\frac{1}{2}$ –*z*) = 3.26(1) Å; Fig. 4], the aromatic skeletons

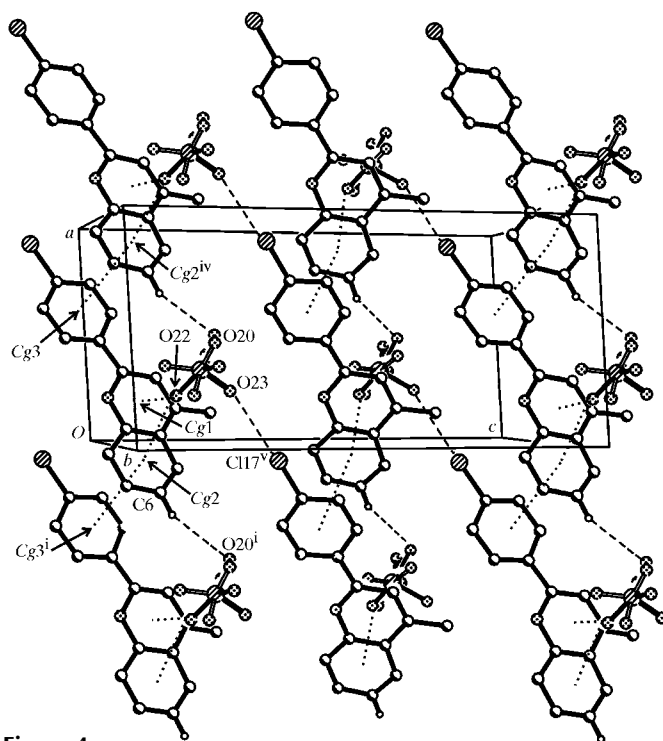


Figure 4

The arrangement of the ions of polymorph (Ib) in the unit cell, viewed along the *b* axis. The C–H···O interactions and O···Cl contacts are represented by dashed lines, and Cl–O··· π and π – π interactions by dotted lines. H atoms not involved in the interactions have been omitted. [Symmetry codes: (i) $x - 1, y, z$; (iv) $1 + x, y, z$; (v) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.]

are at an angle of $66.1(2)^\circ$ (the angle between the mean planes defined by all the atoms of the aromatic skeletons of non-interacting cations), which produces a herring-bone pattern.

The crystal structures of both polymorphs are stabilized by a network of the above-mentioned short-range interactions, as well as by long-range electrostatic interactions between ions.

All interactions demonstrated were found by *PLATON* (Spek, 2003). The C—H...O interactions exhibit a hydrogen-bond-type nature (Steiner, 1999). Interactions between the perchlorate anion or electronegative Cl atom at ring 3, and rings 1 and 2, respectively, identified as Cl—O... π and C—Cl... π interactions, should be of an attractive nature, since the chromenium system is positively charged (Dorn *et al.*, 2005). An attractive nature should also be exhibited by the C—Cl...O(perchlorate) interactions (Allen *et al.*, 1997) identified as O...Cl contacts.

To obtain some idea of how the chromenium (1 and 2) and phenyl (3) rings are mutually oriented in an isolated cation, we optimized the structure at the density functional theory (B3LYP)/6–31G** level (*GAUSSIAN98*; Frisch *et al.*, 1998) and calculated the angle between the mean planes of these fragments. The value obtained was 0.3° , which means that the whole aromatic system is planar. Distortion from planarity of the aromatic system in both polymorphs, apparent in the crystallographic data, may be the cause of their different spectroscopic behaviour.

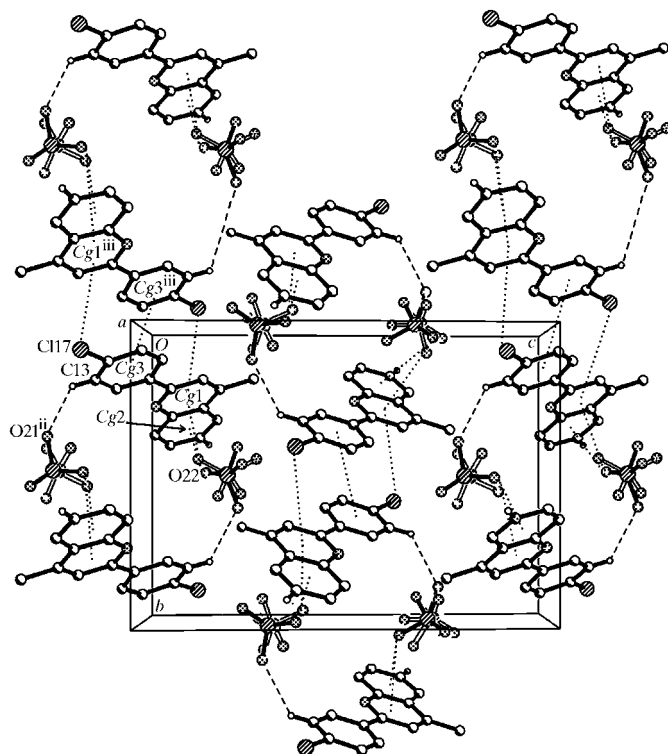


Figure 5
The arrangement of the ions of polymorph (Ib) in the unit cell, viewed along the *a* axis. The C—H...O interactions are represented by dashed lines, and C—Cl... π , Cl—O... π and π — π interactions by dotted lines. H atoms not involved in the interactions have been omitted. [Symmetry codes: (ii) $1 - x, 1 - y, -z$; (iii) $1 - x, -y, -z$.]

Having optimized the structure of the cation, we calculated relative partial charges using natural bond orbital (NBO) analysis (Reed *et al.*, 1988), a Mulliken population analysis (Mulliken, 1955*a,b*) and the electrostatic potential (ESP) fit method (Besler *et al.*, 1990). It is commonly believed that electron deficiency occurs at the ring O atom, but our calculations revealed the reverse situation: there was an excess negative charge at this atom [-0.416 (NBO), -0.488 (Mulliken) and -0.278 (EPS)]. It seems, therefore, that, in this case, traditional assumptions may have to be revised.

Experimental

Compound (I) was synthesized according to a method described in the literature (Czerney *et al.*, 1995). The crude product was purified by recrystallization, initially from concentrated acetic acid and then from dichloromethane. The purity of the compound was confirmed chromatographically and its identity proven by IR and NMR spectroscopy. Crystals of the polymorphic forms (Ia) and (Ib) suitable for X-ray investigations were grown from ethyl acetate and were separated manually.

Polymorph (Ia)

Crystal data

$C_{16}H_{12}ClO^+ \cdot ClO_4^-$	$V = 1584.4(4) \text{ \AA}^3$
$M_r = 355.16$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 11.0290(19) \text{ \AA}$	$\mu = 0.43 \text{ mm}^{-1}$
$b = 12.817(2) \text{ \AA}$	$T = 290(2) \text{ K}$
$c = 11.2083(18) \text{ \AA}$	$0.3 \times 0.3 \times 0.2 \text{ mm}$
$\beta = 90.173(13)^\circ$	

Data collection

Siemens P3/PC diffractometer	$R_{\text{int}} = 0.025$
2915 measured reflections	2 standard reflections
2763 independent reflections	every 98 reflections
2124 reflections with $I > 2\sigma(I)$	intensity decay: 1.5%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	208 parameters
$wR(F^2) = 0.126$	H-atom parameters constrained
$S = 0.92$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
2763 reflections	$\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for polymorph (Ia).

O1—C2	1.326(2)	C2—C11	1.448(3)
O1—C10	1.366(2)	C14—C17	1.733(2)
O1—C2—C3	119.13(18)	C2—O1—C10	122.21(15)
O1—C2—C11	113.14(15)		
O1—C2—C3—C4	1.7(3)	C3—C2—C11—C12	175.5(2)
C2—O1—C10—C9	0.6(3)	C12—C13—C14—C17	-177.48(18)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for polymorph (Ia).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C3—H3...O22	0.93	2.52	3.377(5)	154

Table 3

 Cl—O··· π interactions (\AA , $^\circ$) in polymorph (Ia).

Cg1 is the centroid of the O1/C2—C4/C9/C10 ring and Cg2 is the centroid of the C5—C8/C10/C9 ring.

<i>X</i>	<i>I</i>	<i>J</i>	<i>I</i> ··· <i>J</i>	<i>X</i> ··· <i>J</i>	<i>X</i> — <i>I</i> ··· <i>J</i>
Cl19	O20	Cg1 ⁱ	3.134 (3)	3.684 (2)	101.9 (2)
Cl19	O22	Cg1 ⁱ	3.382 (4)	3.684 (2)	91.7 (2)
Cl19	O22	Cg2 ⁱ	3.427 (4)	4.409 (2)	128.5 (2)
Cl19	O23	Cg1 ⁱ	3.834 (3)	3.684 (2)	73.4 (2)

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

Table 4
 π - π interactions (\AA , $^\circ$) in polymorph (Ia).

 Cg1 is the centroid of the O1/C2—C4/C9/C10 ring and Cg3 is the centroid of the C11—C16 ring. CgI···CgJ is the distance between ring centroids. The dihedral angle is that between the planes of rings *I* and *J*. The interplanar distance is the perpendicular distance of CgI from ring *J*. The offset is the perpendicular distance of ring *I* from ring *J*.

<i>CgI</i>	<i>CgJ</i>	<i>CgI</i> ··· <i>CgJ</i>	Dihedral angle	Interplanar distance	Offset
1	3 ⁱⁱ	3.610 (2)	5.2	3.479 (3)	0.964 (2)
3	1 ⁱⁱ	3.610 (2)	5.2	3.510 (3)	0.844 (2)

 Symmetry code: (ii) $-x, 1 - y, 2 - z$.

Polymorph (Ib)

Crystal data

 $\text{C}_{16}\text{H}_{12}\text{ClO}^+\cdot\text{ClO}_4^-$
 $M_r = 355.16$

 Monoclinic, $P2_1/c$
 $a = 8.0631$ (15) \AA
 $b = 11.873$ (3) \AA
 $c = 16.487$ (2) \AA
 $\beta = 93.292$ (14) $^\circ$
 $V = 1575.8$ (5) \AA^3
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 0.43$ mm^{-1}
 $T = 290$ (2) K

 $0.5 \times 0.4 \times 0.3$ mm

Data collection

Siemens P3/PC diffractometer

2957 measured reflections

2748 independent reflections

 1814 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$

3 standard reflections

every 200 reflections

intensity decay: 2.0%

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.123$
 $S = 0.85$

2748 reflections

255 parameters

261 restraints

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.20$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.26$ e \AA^{-3}
Table 5

 Selected geometric parameters (\AA , $^\circ$) for polymorph (Ib).

O1—C2	1.323 (6)	C2—C11	1.455 (7)
O1—C10	1.376 (6)	C14—Cl17	1.757 (5)
O1—C2—C3	119.7 (5)	C2—O1—C10	121.6 (4)
O1—C2—C11	114.4 (4)		
O1—C2—C3—C4	−1.7 (8)	C3—C2—C11—C12	177.5 (5)
C2—O1—C10—C9	−1.4 (7)	C12—C13—C14—Cl17	−178.6 (5)

Table 6

 Hydrogen-bond geometry (\AA , $^\circ$) for polymorph (Ib).

<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>
C6—H6···O20 ⁱ	0.93	2.60	3.476 (17)	156
C13—H13···O21 ⁱⁱ	0.93	2.50	3.213 (16)	133

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

Table 7

 C—Cl··· π and Cl—O··· π interactions (\AA , $^\circ$) in polymorph (Ib).

Cg1 is the centroid of the O1/C2—C4/C9/C10 ring and Cg2 is the centroid of the C5—C8/C10/C9 ring.

<i>X</i>	<i>I</i>	<i>J</i>	<i>I</i> ··· <i>J</i>	<i>X</i> ··· <i>J</i>	<i>X</i> — <i>I</i> ··· <i>J</i>
C14	Cl17	Cg1 ⁱⁱⁱ	3.941 (2)	4.290 (5)	89.1 (2)
Cl19	O22	Cg1	3.229 (18)	3.854 (9)	106.7 (10)
Cl19	O22	Cg2	3.223 (17)	4.316 (10)	136.0 (10)

 Symmetry code: (iii) $1 - x, -y, -z$.

Table 8
 π - π interactions (\AA , $^\circ$) in polymorph (Ib).

 Cg2 is the centroid of the C5—C8/C10/C9 ring and Cg3 is the centroid of the C11—C16 ring. CgI···CgJ is the distance between ring centroids. The dihedral angle is that between the planes of rings *I* and *J*. The interplanar distance is the perpendicular distance of CgI from ring *J*. The offset is the perpendicular distance of ring *I* from ring *J*.

<i>CgI</i>	<i>CgJ</i>	<i>CgI</i> ··· <i>CgJ</i>	Dihedral angle	Interplanar distance	Offset
2	3 ⁱ	3.713 (3)	2.2	3.409 (3)	1.464 (3)
3	2 ^{iv}	3.713 (3)	2.2	3.464 (3)	1.336 (3)
3	3 ⁱⁱⁱ	4.007 (3)	0.0	3.441 (3)	2.054 (3)

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

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, or with C—H = 0.96 \AA and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methyl group. The atoms of the perchlorate anion in polymorph (Ib) were located in a difference Fourier map and refined to an ideal tetrahedron, with restrained standard deviations of 0.01 and 0.03 \AA for the Cl—O and O···O distances, respectively (SADI instruction in *SHELXL97*; Sheldrick, 1997) (Müller *et al.*, 2006). Following refinement, the anisotropic displacement parameters of adjacent atoms were restrained to be similar (SIMU instruction), and the main directions of movements of covalently bonded atoms were likewise restrained (DELU instruction) (Müller *et al.*, 2006). The occupancy ratio was determined by isotropic refinement for the disordered site and was refined freely during subsequent anisotropic refinement.

For both compounds, data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3073). Services for accessing these data are described at the back of the journal.

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