Di-μ-halogeno-bis[halogeno(triphenylphosphine)mercury(II)], [Ph₃PHg*X*-(μ-*X*)₂*X*HgPPh₃], reinvestigated at 120 K for *X* = Cl and Br, and a second polymorph for *X* = I, also at 120 K

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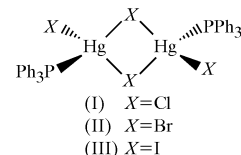Correspondence e-mail: cg@st-andrews.ac.uk

Di-μ-chloro-bis[chloro(triphenylphosphine)mercury(II)], [Hg₂Cl₄(C₁₈H₁₅P)₂], (I), and di-μ-bromo-bis[bromo(triphenylphosphine)mercury(II)], [Hg₂Br₄(C₁₈H₁₅P)₂], (II), have been reinvestigated at 120 K. The molecules of (I) lie across inversion centres in space group $P2_1/n$, and in both (I) and (II) the complexes are linked into three-dimensional frameworks by a combination of C—H···*X* (*X* = Cl and Br) and C—H···π(arene) hydrogen bonds. At 120 K, di-μ-iodo-bis[iodo(triphenylphosphine)mercury(II)], [Hg₂I₄(C₁₈H₁₅P)₂], (III), crystallizes as a new polymorphic form having $Z' = \frac{1}{2}$, where the complexes lie across inversion centres in space group $P2_1/n$; the complexes are linked into sheets by a combination of C—H···I and C—H···π(arene) hydrogen bonds. In the $Z' = 1$ polymorph of this compound, a single C—H···I hydrogen bond generates simple chains.

Comment

The structures of the title compounds, Ph₃PHg*X*(μ₂-*X*)₂-*X*HgPPh₃] [*X* = Cl for (I), Br for (II) and I for (III)], were first reported some years ago. For *X* = Cl (Bell *et al.*, 1980), the structure was refined to *R* = 0.083 using diffraction data collected at ambient temperature. Only Hg, Cl and P atoms were refined anisotropically, and the phenyl rings were all constrained to be rigid hexagons; no H atoms were included in the refinement. A very similar refinement was used for *X* = Br (Bowmaker *et al.*, 1993), although in this case H atoms were included in calculated positions, giving a final *R* value of 0.070. The use of ambient-temperature diffraction data for *X* = I (Bell *et al.*, 1989) allowed anisotropic refinement of most of the C atoms, although several remained isotropic, possibly indicating some difficulties with the refinement, which termi-

nated at *R* = 0.094. There is an otherwise unpublished set of coordinates for this same compound (Dix & Jones, 1997) deposited in the Cambridge Structural Database (CSD; Allen, 2002; refcode JAHCOK01), based on a refinement using diffraction data collected at 173 K and giving *R* = 0.056. For each of (I)–(III), the gross structure of the complex is similar, containing halogen-bridged dimers which are crystallographically centrosymmetric for *X* = Cl and approximately centrosymmetric for *X* = Br or I; however, none of the published reports identified any supramolecular aggregation beyond the formation of the halogen-bridged dimers.

(I) *X*=Cl
(II) *X*=Br
(III) *X*=I

We have now taken the opportunity to redetermine the structures of (I)–(III) using data collected at 120 K. For (I) and (II), we find the same phases at 120 K as those previously reported at ambient temperature. It is clear that in both structures there are significant C—H···π(arene) and C—H···*X* (*X* = Cl and Br) hydrogen bonds, which together link the dimeric complexes into continuous three-dimensional framework structures. On the other hand, for (III), we find a different phase from that reported previously. The previous reports (Bell *et al.*, 1989; Dix & Jones, 1997) describe a monoclinic structure having *Z* = 4 and *Z'* = 1 at both 298 and 173 K, which is, in fact, isostructural with (II).

We find here for (III) a different monoclinic structure at 120 K, with *Z* = 2 and $Z' = \frac{1}{2}$, whose unit-cell dimensions are similar to those of (I), but whose overall structure mimics the mirror image of (I) (Figs. 1 and 2). In this $Z' = \frac{1}{2}$ phase of (III),
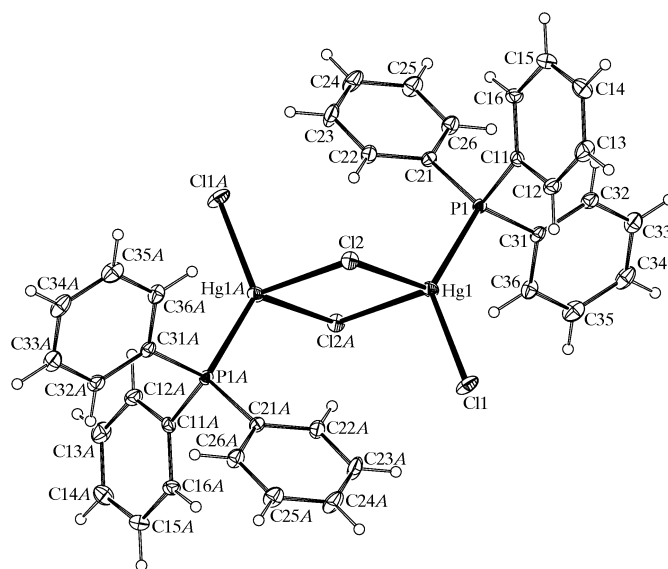

Figure 1
The dimeric molecular unit in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and atoms labelled with the suffix *A* are at the symmetry position (1 − *x*, 1 − *y*, 1 − *z*).

the centrosymmetric dimers are linked into sheets by a combination of C—H···π(arene) and C—H···I hydrogen bonds and an aromatic π–π stacking interaction.

For both (I), where we have refined the structure without any of the constraints applied earlier (Bell *et al.*, 1980), and (III), the precision is significantly better than reported previously. Thus, for example, for both (I) and the $Z' = 1$ polymorph of (III), the previously reported s.u. values for the P—C bonds are 0.02–0.03 Å (Bell *et al.*, 1980, 1989), whereas from the present refinements of (I) and the $Z' = \frac{1}{2}$ polymorph of (III), these s.u. values are 0.003 and 0.004 Å, respectively (Tables 1 and 3). In addition, the R values are very much lower for the present refinements of (I) and (III). In each of (I) and (III), the long bridging Hg—X bonds (X = Cl and I) (Tables 1 and 3) may be indicative of significant ionic character in these bonds.

As in the published report on the bromo complex (II), some difficulty was experienced even using data collected at 120 K, and attempts to refine the C atoms anisotropically consistently led to unacceptable displacement ellipsoids, although refinements with these atoms assigned isotropic displacement parameters appeared to be satisfactory. Accordingly, we do not discuss this structure in detail, beyond confirming that the same phase occurs at 120 K as at ambient temperature and noting that the dimeric complexes are linked into a three-dimensional framework by hydrogen bonds.

In compound (I) (Fig. 1), atoms C24 at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, which are both components of the complex centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, act as hydrogen-bond donors (Table 2) to the C31–C36 aryl rings at $(\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, respectively, which themselves are components of the complexes centred at $(1, 0, 0)$ and $(0, 1, 1)$, respectively. Similarly, the C31–C36 aryl rings at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ accept hydrogen bonds from atoms C24 at $(-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, which lie in the complexes centred at $(0, 0, 1)$ and $(1, 1, 0)$, respectively. By this means, the
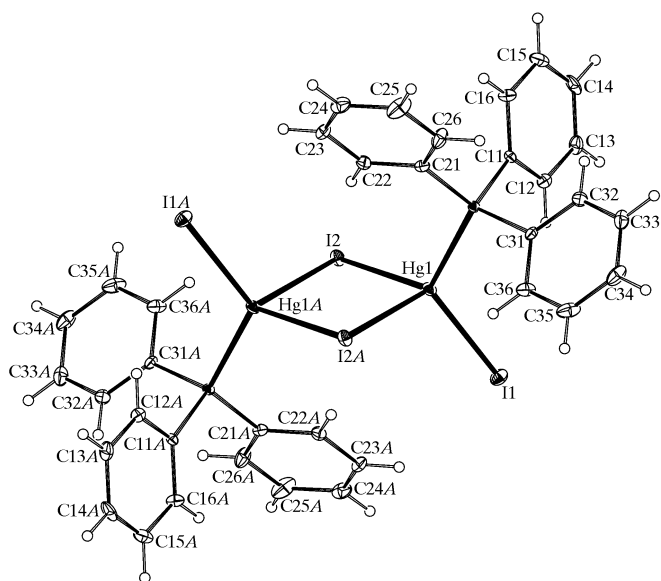

Figure 2
The dimeric molecular unit in (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and atoms labelled with the suffix A are at the symmetry position $(1 - x, 1 - y, 1 - z)$.
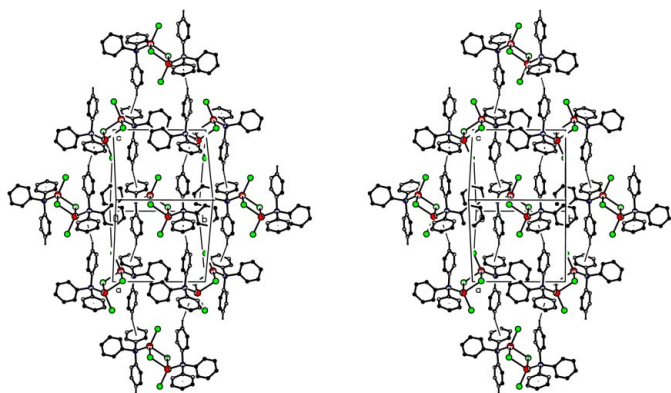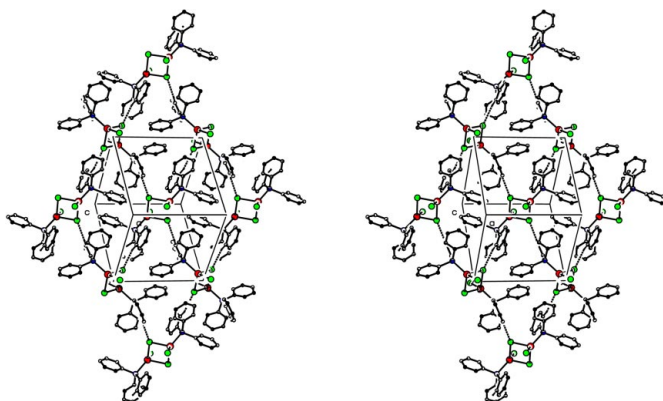

Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of a (10$\bar{1}$) sheet generated by a single C—H···Cl hydrogen bond. For clarity, H atoms not involved in the motif shown have been omitted.

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a (101) sheet generated by a single C—H···π(arene) hydrogen bond. For clarity, H atoms not involved in the motif shown have been omitted.
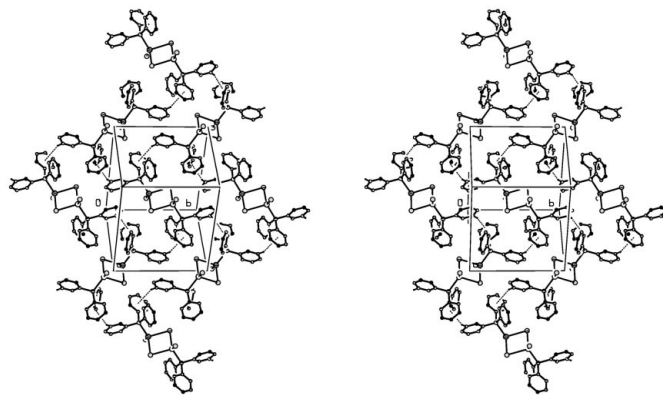

Figure 5
A stereoview of part of the crystal structure of (III), showing the formation of a (101) sheet generated by a single C—H···π(arene) hydrogen bond. For clarity, H atoms not involved in the motif shown have been omitted.

dimeric complexes are linked by a single C—H⋯π(arene) hydrogen bond into sheets lying parallel to (101) (Fig. 3)

There is a single π–π stacking interaction in the structure of (I), which serves to reinforce the (101) sheet. The C11–C16 rings in the molecules at (x, y, z) and $(1 - x, -y, 1 - z)$, which lie in the same sheet, are parallel, with an interplanar spacing of 3.539 (2) Å; the ring-centroid separation is 3.782 (2) Å, corresponding to a near-ideal centroid offset of 1.334 (2) Å. In addition, there are a number of fairly short C—H⋯Cl interactions whose H⋯Cl distances are well within the van der Waals sum (Bondi, 1964; Nyburg & Faerman, 1985; Navon et al., 1997) and which can therefore be regarded as weak hydrogen bonds (Table 2). Two of the three C—H⋯Cl hydrogen bonds lie within a single (101) sheet, thus providing further reinforcement of the sheet, while the third such bond serves to generate a (10$\bar{1}$) sheet.

Atoms C26 at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ act as donors to atoms Cl2 at $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, respectively, which form parts of the dimeric complexes centred at $(0, 0, 0)$ and $(1, 1, 1)$. In like manner, atoms Cl2 at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ accept hydrogen bonds from atoms C26 at $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, respectively, which are themselves components of the dimers centred at $(1, 0, 1)$ and $(0, 1, 0)$, so forming a (10$\bar{1}$) sheet (Fig. 4). The combination of the (101) and (10$\bar{1}$) sheets, each generated by a single hydrogen bond, is sufficient to link all of the dimers into a single three-dimensional framework structure.

In compound (III) (Fig. 2), the supramolecular aggregation involves C—H⋯π(arene) and C—H⋯I hydrogen bonds (Table 4), augmented by a weak π–π stacking interaction, just as in (I), but the supramolecular structure is strictly two-dimensional, unlike that of (I). Atom C15 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the C31–C36 ring at $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, which lies in the dimer centred at $(0, 0, 1)$; propagation by the space group of this interaction then generates a (101) sheet (Fig. 5), similar to that formed in (I). The single C—H⋯I hydrogen bond lies within this sheet, although its participants do not mimic those of either of the intrasheet C—H⋯Cl hydrogen bonds in (I). The C11–C16 rings in the molecules at (x, y, z) and $(1 - x, -y, 1 - z)$, which lie in the same sheet, are parallel, with an interplanar spacing of 3.368 (3) Å, much smaller than the corresponding spacing in (I); the ring-centroid separation of 3.850 (3) Å is significantly larger than the corresponding distance in (I), and the ring-centroid offset is 1.865 (3) Å, indicating only a weak interaction. There are thus no direction-specific interactions between adjacent (101) sheets in (III).

In the $Z' = 1$ polymorph of (III) (CSD refcode JAHCO-K01), reanalysis of the atom coordinates at 173 K (Dix & Jones, 1997) shows that C—H⋯π(arene) and aromatic π–π stacking interactions are both absent, and that the dimers are linked by a single C—H⋯I hydrogen bond into chains running parallel to the [001] direction and generated by the c-glide planes (Fig. 6)

Experimental

For the preparation of compounds (I)–(III), an excess of triphenylphosphonium fluorenylide in CHCl₃ solution was added dropwise at 273 K to a solution of the appropriate mercury(II) halide, also in chloroform, with a molar ratio of ylide to mercury in the range 1 to 2, and this mixture was then stirred at 303 K for 3 h. The solvent was removed and the solid residue was dissolved in dry tetrahydrofuran; after several days at 273 K, crystals suitable for single-crystal X-ray diffraction were obtained.
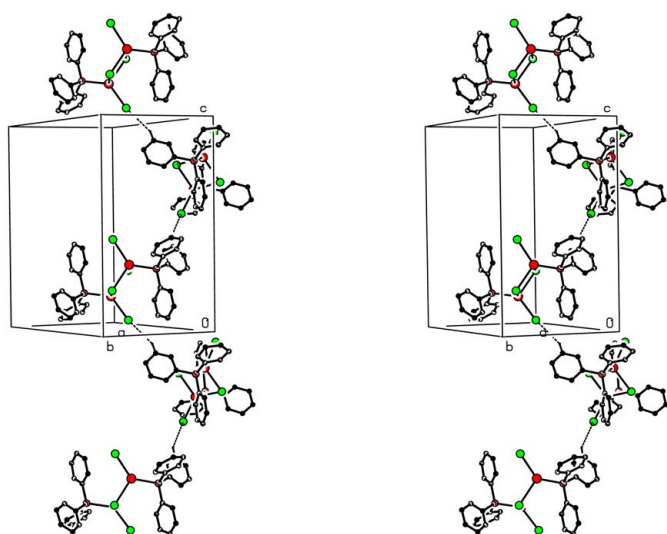

Figure 6
A stereoview of part of the crystal structure of JAHCOK01 (Dix & Jones, 1997), showing the formation of a [001] chain generated by a single C—H⋯I hydrogen bond. The original atom coordinates have been employed; for clarity, H atoms not involved in the motif shown have been omitted.

Compound (I)

Crystal data

[Hg₂Cl₄(C₁₈H₁₅P)₂]	$D_x = 1.945$ Mg m⁻³
$M_r = 1067.52$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4163
$a = 12.1540$ (2) Å	reflections
$b = 11.2982$ (3) Å	$\theta = 3.4$–27.5°
$c = 13.2965$ (3) Å	$\mu = 8.82$ mm⁻¹
$\beta = 93.3460$ (16)°	$T = 120$ (2) K
$V = 1822.74$ (7) Å³	Block, colourless
$Z = 2$	$0.29 \times 0.24 \times 0.18$ mm

Data collection

Nonius KappaCCD diffractometer	3593 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.042$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(SADABS; Sheldrick, 2003)	$h = -15 \rightarrow 14$
$T_{min} = 0.095$, $T_{max} = 0.206$	$k = -14 \rightarrow 14$
28 163 measured reflections	$l = -17 \rightarrow 17$
4163 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0178P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.024$	$+ 1.6853P]$
$wR(F^2) = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
4163 reflections	$\Delta\rho_{max} = 0.68$ e Å⁻³
199 parameters	$\Delta\rho_{min} = -1.02$ e Å⁻³
H-atom parameters constrained	

metal-organic compounds

Table 1
Selected interatomic distances (Å) for (I).

Hg1—Cl1	2.4015 (8)	P1—C11	1.801 (3)
Hg1—Cl2	2.6101 (8)	P1—C21	1.807 (3)
Hg1—Cl2^i	2.6506 (8)	P1—C31	1.812 (3)
Hg1—P1	2.3991 (8)		

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

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

$Cg3$ is the centroid of ring C31–C36.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
C13—H13$\cdots$Cl1^{ii}	0.95	2.81	3.720 (4)	161
C15—H15$\cdots$Cl2^{iii}	0.95	2.83	3.520 (3)	131
C26—H26$\cdots$Cl2^{iv}	0.95	2.76	3.605 (4)	148
C24—H24$\cdots$Cg3^{v}	0.95	2.74	3.610 (4)	153

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

Compound (III)

Crystal data

[Hg$_2$I$_4$(C$_{18}$H$_{15}$P)$_2$]	$D_x = 2.415$ Mg m^{-3}
$M_r = 1433.32$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4516
$a = 11.4078$ (2) Å	reflections
$b = 12.4980$ (4) Å	$\theta = 3.6$–27.5°
$c = 13.9124$ (4) Å	$\mu = 11.01$ mm^{-1}
$\beta = 96.3270$ (17)°	$T = 120$ (2) K
$V = 1971.47$ (9) Å^3	Block, colourless
$Z = 2$	$0.35 \times 0.26 \times 0.24$ mm

Data collection

Nonius KappaCCD diffractometer	3935 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.036$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
($SADABS$; Sheldrick, 2003)	$h = -14 \rightarrow 14$
$T_{min} = 0.041$, $T_{max} = 0.071$	$k = -15 \rightarrow 16$
24 795 measured reflections	$l = -18 \rightarrow 18$
4516 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$+ 2.7697P]$
$wR(F^2) = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{max} = 0.002$
4516 reflections	$\Delta\rho_{max} = 0.70$ e Å^{-3}
199 parameters	$\Delta\rho_{min} = -1.31$ e Å^{-3}
H-atom parameters constrained	

Table 3
Selected interatomic distances (Å) for (III).

Hg1—I1	2.6977 (3)	P1—C11	1.804 (4)
Hg1—I2	2.8422 (3)	P1—C21	1.808 (4)
Hg1—I2^i	2.9863 (3)	P1—C31	1.816 (4)
Hg1—P1	2.4724 (10)		

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

For compounds (I)–(III), the space groups $P2_1/n$, $P2_1/c$ and $P2_1/n$, respectively, were uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as

Table 4
Hydrogen-bond geometry (Å, °) for (III).

$Cg3$ is the centroid of ring C31–C36.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
C14—H14$\cdots$I2^{iii}	0.95	3.04	3.952 (4)	161
C15—H15$\cdots$Cg3^{ii}	0.95	2.89	3.770 (5)	154

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

riding, with C—H distances of 0.95 Å and U_{iso}(H) values of $1.2U_{eq}$(C). For (II), the refinement proceeded in an apparently satisfactory manner, with individual isotropic displacement parameters for the C atoms, to $R = 0.051$ and $wR_2 = 0.110$ for 217 parameters and 6070 and 8349 data, respectively, but attempts to refine the C atoms anisotropically led to unacceptable displacement ellipsoids.

For compounds (I) and (III), data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; structure solution: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); structure refinement: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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