Diphenylmercury, redetermined at 120 K: sheets built from a single C—H···π(arene) hydrogen bond

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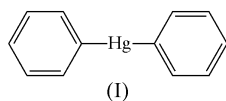RJ, Brazil

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At 120 K, the molecules of the title compound, $[Hg(C_6H_5)_2]$,
lie across centres of inversion in space group $P2_1/n$ and are
linked by a single C—H···π(arene) hydrogen bond into (101)
sheets. The same supramolecular structure is found at 298 K.

Comment

The structure of diphenylmercury, (I), was first successfully
analysed only in 1977 (Grdenić *et al.*, 1977), despite numerous
earlier attempts (Kitaigorodsky & Grdenić, 1948; Ziólkowska,
1962; Ziólkowska *et al.*, 1964), which had been hampered by a
combination of inadequate absorption corrections and the
occurrence of twinning. Using diffraction data collected at
ambient temperature, an *R* value of 0.023 was achieved with
725 unweighted data and with H atoms included in the
calculations with C—H distances in the range 0.93–1.02 Å
(Grdenić *et al.*, 1977). The structure consisted of nearly planar
centrosymmetric molecules; although a number of fairly short
C···C, C···H and H···H intermolecular contacts were
recorded, the consequences of these were not analysed. Our
reanalysis, using *PLATON* (Spek, 2003), of the published
structure using atomic coordinates retrieved from the
Cambridge Structural Database (Allen, 2002; refcode
DIPHHG11) found no direction-specific intermolecular
interactions.

(I)

We have now reinvestigated the structure of (I) using a
larger data set collected at 120 K; in addition, we collected a
data set at 298 K, and the same phase was found. Although,
for the sake of convenience and the much lower β angle, we
have chosen to refine the structure in space group $P2_1/n$,

rather than the alternative $P2_1/c$, as employed by Grdenić *et al.*
(1977), we also solved the structure in $P2_1/c$. It was evident,
from both the cell dimensions and the atom coordinates in
$P2_1/c$ that the same phase was employed in this study as in the
earlier one. The structure of (I) determined at 120 K has
better precision than that reported at ambient temperatures.
Thus, the s.u. values on the Hg—C and C—C distances
(Table 1) are less than half of those reported previously
(0.007 Å for Hg—C and 0.010–0.014 Å for C—C). Despite the
larger data set used here, at 120 K, the conventional *R* value is
significantly lower than the previous ambient-temperature
value (0.023).

We find at 120 K, centrosymmetric molecules (Fig. 1) with
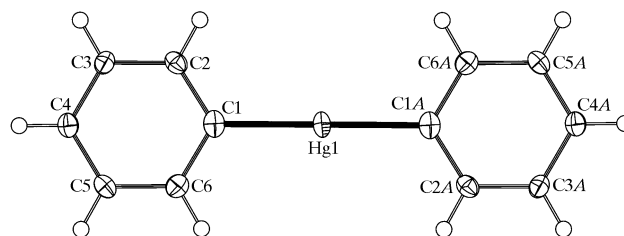an interplanar spacing of 0.222 (4) Å, consistent with the

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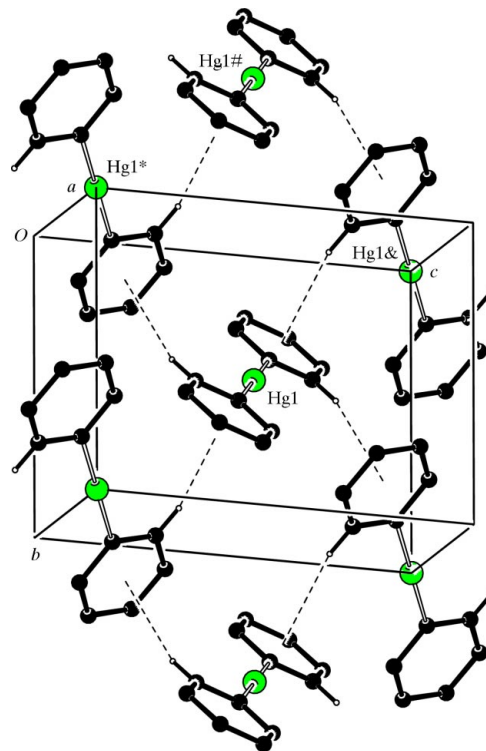the suffix *A* are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

Figure 2
Part of the crystal structure of (I), showing a (101) sheet formed from the
action of a C—H···π(arene) hydrogen bond. Hg atoms marked with an
asterisk (*), a hash (#) or an ampersand (&) are at the positions (1, 0, 0),
$(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$ and (0, 0, 1), respectively. For the sake of clarity, H atoms not
involved in the motif shown have been omitted.

structure previously reported at ambient temperature. However, these molecules are linked into sheets by a single nearly linear C—H···π(arene) hydrogen bond (Table 2). With the reference molecule centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, atoms C6 at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ act as hydrogen-bond donors to the aryl rings at $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ and $(-\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$, respectively, which form parts of the molecules centred at $(1, 0, 0)$ and $(0, 1, 1)$, respectively. Similarly, the aryl rings at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ accept hydrogen bonds from atoms C6 at $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ and $(-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, respectively, which form parts of the molecules centred at $(1, 1, 0)$ and $(0, 0, 1)$. In this way, the molecules are linked into (101) sheets (Fig. 2), although there are no direction-specific interactions between adjacent sheets.

We find precisely the same supramolecular aggregation at 298 K, and the question then arises why this aggregation is not apparent from the coordinates reported by Grdenić *et al.* (1977). The explanation appears to lie in the location of the H atoms in the earlier structure. The authors stated that 'the H atoms were included in the structure-factor calculations with the isotropic thermal parameters of the bonded C atoms, but the parameters were not refined' (Grdenić *et al.*, 1977); however, at no point did the authors specify how the H atoms were actually located or what constraints were applied to their positions during the refinement. In fact, analysis of their H-atom coordinates shows that many of these atoms are significantly displaced from the plane of the aryl ring; in particular, the two calculated C—C—C—H torsion angles for the H atom bonded to atom C6 are 168 and −169°. In addition, the two exocyclic C—C—H angles at atom C6 are 116 and 123°, and it seems probable that the erroneous location of the H atom bonded to atom C6 has previously obscured the occurrence of the C—H···π(arene) hydrogen bond.

Experimental

The title compound was isolated from the reaction between mercury(II) chloride and methyltriphenyltin(IV) (2:1 molar ratio) in ethanol. Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethanol.

Crystal data

[Hg(C6H5)2]	$D_x = 2.458$ Mg m^{-3}
$M_r = 354.79$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 1098
$a = 5.6222$ (3) Å	reflections
$b = 8.0912$ (4) Å	$\theta = 3.2$–27.5°
$c = 10.5852$ (5) Å	$\mu = 16.00$ mm^{-1}
$\beta = 95.485$ (3)°	$T = 120$ (2) K
$V = 479.32$ (4) Å^3	Plate, colourless
$Z = 2$	$0.28 \times 0.12 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer	837 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.034$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(*SADABS*; Sheldrick, 2003)	$h = -7 \rightarrow 7$
$T_{min} = 0.088$, $T_{max} = 0.527$	$k = -10 \rightarrow 10$
7117 measured reflections	$l = -13 \rightarrow 13$
1098 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0209P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.017$	$+ 0.2975P]$
$wR(F^2) = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} < 0.001$
1098 reflections	$\Delta\rho_{max} = 0.71$ e Å^{-3}
62 parameters	$\Delta\rho_{min} = -0.87$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.0133 (8)

Table 1
Selected geometric parameters (Å).

Hg1—C1	2.088 (3)	C4—C5	1.383 (5)
C1—C2	1.393 (5)	C5—C6	1.398 (5)
C2—C3	1.384 (5)	C6—C1	1.400 (5)
C3—C4	1.402 (5)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···Cg^i	0.95	2.84	3.759 (4)	164

Symmetry code: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$. Note: Cg is the centroid of the C1–C6 ring.

All H atoms were located from difference maps and then treated as riding, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection, cell refinement and data reduction: *COLLECT* (Hooft, 1999) and *DENZO* (Otwinowski & Minor, 1997); 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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