

## A new polymorph and two inclusion compounds of 9,9'-spirobifluorene

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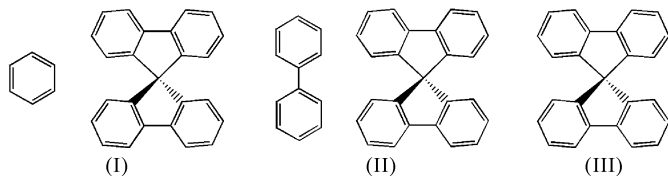
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Received 9 February 2005  
 Accepted 24 March 2005  
 Online 30 April 2005

Two new inclusion compounds of 9,9'-spirobifluorene (SBF) incorporating benzene [(I), C<sub>25</sub>H<sub>16</sub>·C<sub>6</sub>H<sub>6</sub>] and biphenyl [(II), C<sub>25</sub>H<sub>16</sub>·C<sub>12</sub>H<sub>10</sub>], and a new polymorph of SBF [(III), C<sub>25</sub>H<sub>16</sub>] are reported. All three exhibit C—H···π(arene) hydrogen bonds between adjacent SBF molecules. Compound (II) also contains biphenyl C—H to SBF π-arene interactions. Collectively, hydrogen bonding gives rise to a chain and a layered motif in compounds (I) and (II), respectively.

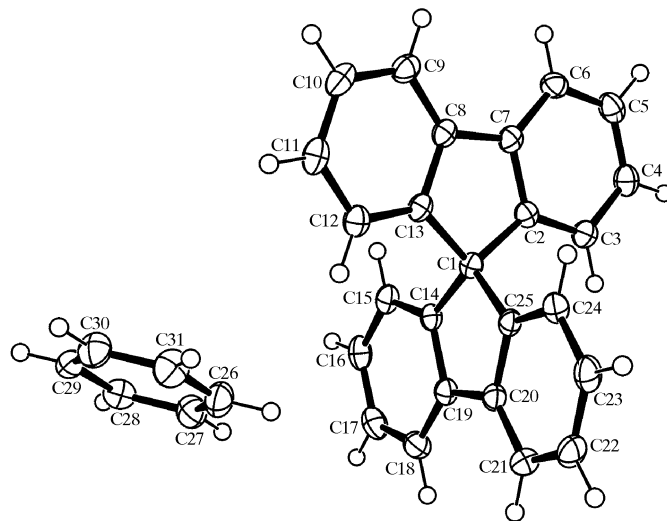
### Comment

The synthesis of 9,9'-spirobifluorene (SBF) was first reported by Clarkson & Gomberg in 1930, and the first single-crystal structure determination was reported four decades later by Schenk (1972). Exhibiting *D*<sub>2d</sub> point symmetry, SBF is an unusual structural motif, which has prompted its use in molecular recognition (Alcazar & Diederich 1992) and catalytic applications (Poriel *et al.*, 2003), and its incorporation into materials that exhibit unusual optoelectronic properties (Wong *et al.*, 2002). We have recently been interested in using SBF as a structural motif in molecular solids and report here the structures of two inclusion compounds, (I) and (II), incorporating benzene and biphenyl, respectively. In the course of our study, we also determined the structure of a new polymorph of SBF, (III).

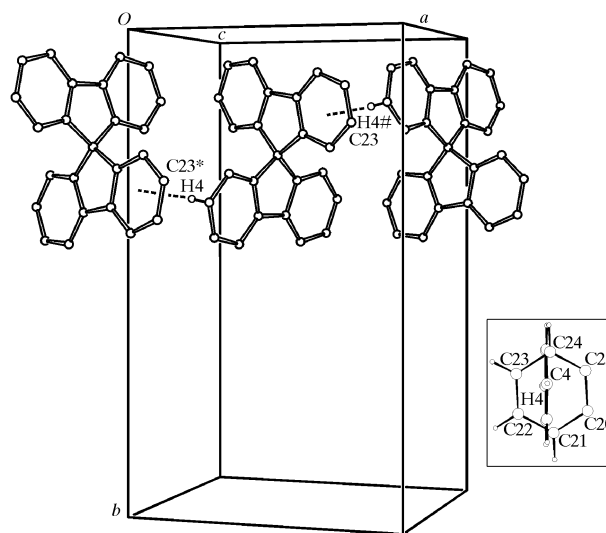


One of our initial aims had been to prepare co-crystals of SBF and fluorinated aromatics, including hexafluorobenzene, perfluoronaphthalene and perfluorobiphenyl, with the intention of investigating supramolecular structures akin to those derived from co-crystallization between planar hydro- and fluoroaromatics. However, in no case did co-crystals between SBF and fluoroaromatics result. We tentatively assigned this

observation to repulsive (steric) interactions between SBF and fluoroaromatics, preventing the attractive molecular electric quadrupole moment interactions that result in parallel stacking in many perhydro/perfluoro aromatic co-crystals (Williams, 1993). However, we rationalized that it may be possible to prepare inclusion compounds incorporating SBF and hydroaromatics, because the relative quadrupole moments would give rise to attractive edge-to-face electrostatic interactions (Lowden & Chandler 1974; Shi & Bartell 1988) that could be sterically accessible for SBF. Indeed, co-crystallization of SBF and the hydroaromatics benzene and biphenyl gave the inclusion compounds (I) and (II), respec-



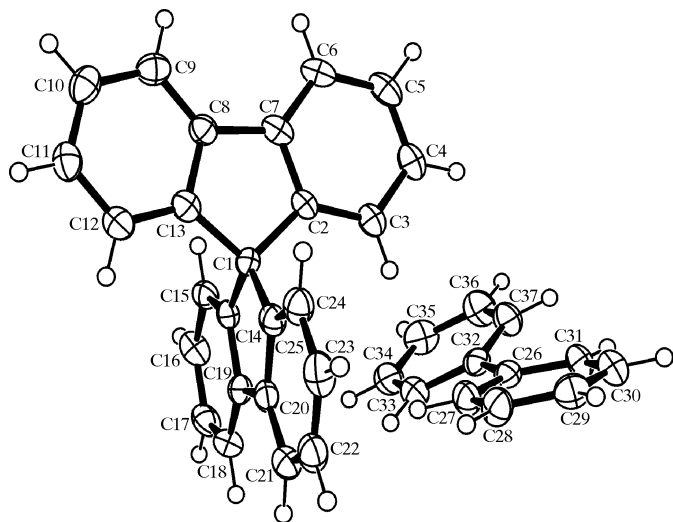
**Figure 1**  
 A view of the asymmetric unit of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids.



**Figure 2**  
 The hydrogen bonding in (I). Atoms marked with an asterisk (\*) or a hash (#) are at the symmetry positions ( $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ) and ( $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ), respectively. Inset: a view down the C4—H4 bond axis, showing the relative π-arene position.

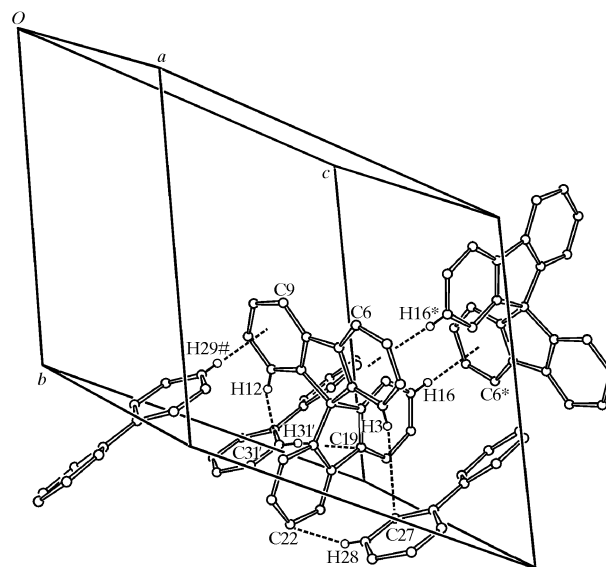
tively, which exhibit a range of edge-to face C—H··· $\pi$ (arene) hydrogen bonds between the aromatic moieties.

The bond lengths and angles of the constituent molecules of (I)–(III) are not exceptional. Examination of the packing diagrams reveals structural motifs resulting from C—H··· $\pi$ (arene) interactions and, based on the C—H··· $A$  ( $A$  = acceptor) angles and H··· $A$  bond lengths, these are considered here as weak hydrogen bonds.

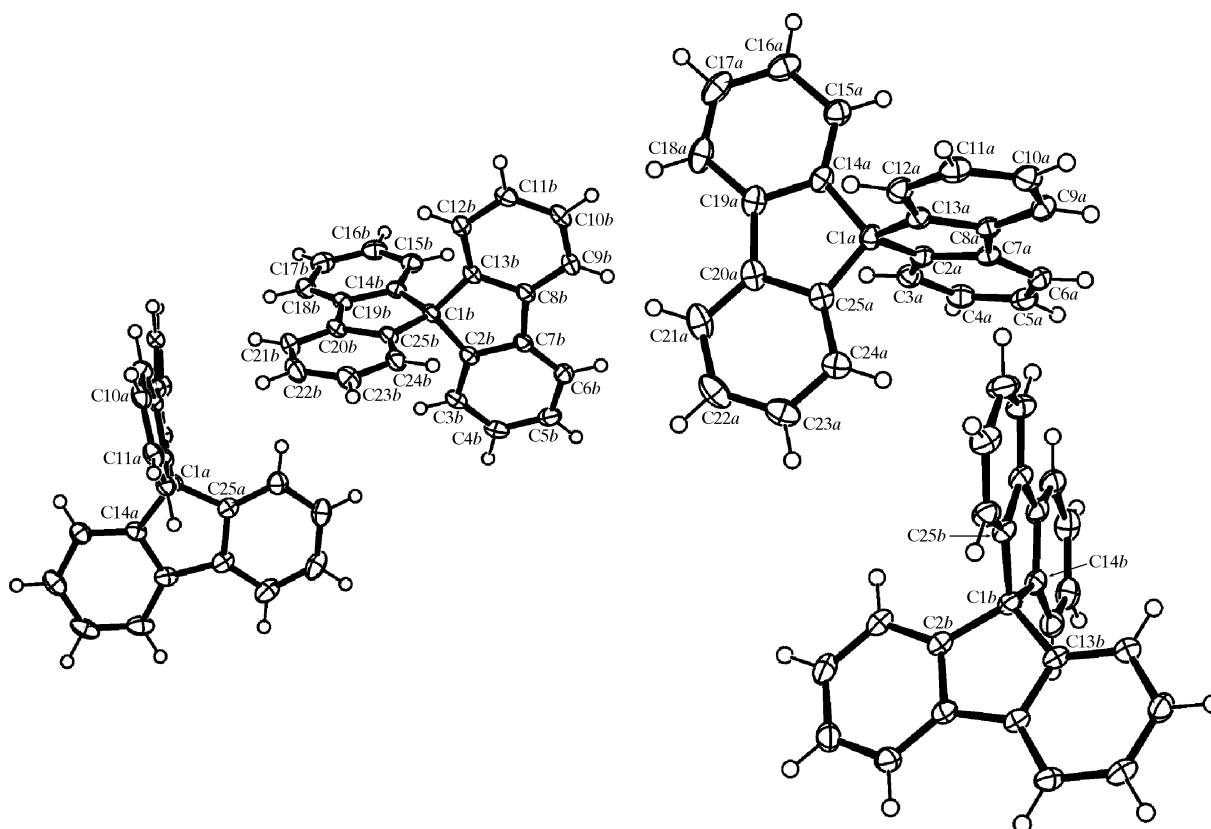


**Figure 3**  
A view of the asymmetric unit of (II), showing the atom-numbering scheme and 50% probability displacement ellipsoids.

Compound (I) contains one molecule of SBF and one molecule of benzene in the asymmetric unit (Fig. 1). Hydrogen bonds are present between adjacent SBF molecules, resulting in an infinite chain motif (Fig. 2). The benzene molecules do not participate in any directional bonding, and there is no



**Figure 4**  
The hydrogen bonding in (II). Atoms marked with an asterisk (\*), a hash (#) or a prime (') are at the symmetry positions  $(1-x, 1-y, 2-z)$ ,  $(1-x, 2-y, -z)$  and  $(-1+x, y, z)$ , respectively.



**Figure 5**  
A view of the asymmetric unit of (III), showing both SBF moieties and the atom-numbering scheme, with 50% probability displacement ellipsoids.

directional bonding nor any short contacts between the chains. Hydrogen-bonding details are shown in Fig. 2, and the distance between atom H4 in the molecule at  $(x, y, z)$  and Cg1 (the centroid of the C20–C25 benzene ring) in the symmetry-related molecule at  $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$  is 2.67 Å (Table 1).

Compound (II) contains one molecule of SBF and one molecule of biphenyl in the asymmetric unit (Fig. 3) and exhibits several C–H... $\pi$ (arene) hydrogen-bonding motifs (Fig. 4), which collectively result in a layered structure with planes parallel to the (011) direction (Table 2). In contrast with (I), adjacent SBF molecules at  $(x, y, z)$  and  $(1 - x, 1 - y, 2 - z)$  are connected *via* a pair of hydrogen bonds between atom H16 and the C2–C7 benzene ring (Fig. 4), with a H16...Cg2 (ring centroid of the C2–C7 ring) distance of 2.65 Å. Biphenyl distance of molecules connect SBF pairs *via* a series of C–H... $\pi$ -arene interactions. Atom H29 in a biphenyl molecule at  $(1 - x, 2 - y, 1 - z)$  interacts in an asymmetric hydrogen bond with the arene moiety C8–C13 (centroid Cg3) of an SBF molecule at  $(x, y, z)$ . In addition, biphenyl–SBF hydrogen bonding is present between atoms H3 and C27 of an SBF molecule at  $(x, y, z)$ , and atoms C22 and H28, respectively, of a biphenyl molecule at  $(x, y, z)$ , connecting pairs of SBF molecules into a chain motif. The chains can then be interpreted as precursors to a layer in the [011] plane *via* interaction of SBF and biphenyl atoms.

Compound (III) contains two molecules of SBF in the asymmetric unit (Fig. 5), in contrast to a single molecule observed by Schenk (1971), which aggregates through very short intermolecular C–C distances (3.22, 3.35 and 3.45 Å) from edge–edge  $\pi$ -interactions between phenyl groups. The new polymorph, (III), does not exhibit short C–C contacts, but SBF molecules of (III) participate in C–H... $\pi$  interac-

tions to give centrosymmetric SBF dimers (Fig. 6), with a H11A...Cg4 distance of 2.59 Å [Cg4 is the centroid of the C20A–C25A ring at  $(1 - x, -y, 1 - z)$ ; C11A–H11A = 0.95 Å, C11A...Cg4 = 3.495 Å and C11A–H11A...Cg4 = 160°]. Examination of the packing shows that layers of discrete SBF dimers are present parallel to the *bc* plane, separated by layers of SBF molecules that do not exhibit directional bonding (Fig. 6). In our study, all other solvent mixtures that we examined led to crystallization of the polymorph identified by Schenk (1971). This suggests that polymorph (III) is possibly metastable with respect to that described by Schenk (1971).

It is anticipated that the weak hydrogen-bonding motifs observed in compounds (I)–(III) are likely to be an important factor in determining the structures of molecular solids derived from SBF.

### Experimental

Single crystals of (I)–(III) were grown by slow evaporation of SBF (20 mg) dissolved in benzene for (I), in pentane containing 1 equivalent of biphenyl for (II), and in a 1:1 mixture of hexafluorobenzene and dichloromethane for (III). All compounds melted in the range 470–473 K.

#### Compound (I)

##### Crystal data

C <sub>25</sub> H <sub>16</sub> ·C <sub>6</sub> H <sub>6</sub>	$D_x = 1.219 \text{ Mg m}^{-3}$
$M_r = 394.49$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4471 reflections
$a = 10.7900 (6) \text{ \AA}$	$\theta = 2.2\text{--}27.4^\circ$
$b = 18.4004 (10) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$c = 10.8403 (6) \text{ \AA}$	$T = 115 (2) \text{ K}$
$\beta = 92.8770 (10)^\circ$	Block, colourless
$V = 2149.5 (2) \text{ \AA}^3$	$0.2 \times 0.2 \times 0.2 \text{ mm}$
$Z = 4$	

##### Data collection

Bruker SMART CCD area-detector diffractometer	4921 independent reflections
$\varphi$ and $\omega$ scans	3949 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$R_{\text{int}} = 0.024$
$T_{\text{min}} = 0.893, T_{\text{max}} = 0.990$	$\theta_{\text{max}} = 27.5^\circ$
14 724 measured reflections	$h = -14 \rightarrow 13$
	$k = -23 \rightarrow 23$
	$l = -14 \rightarrow 12$

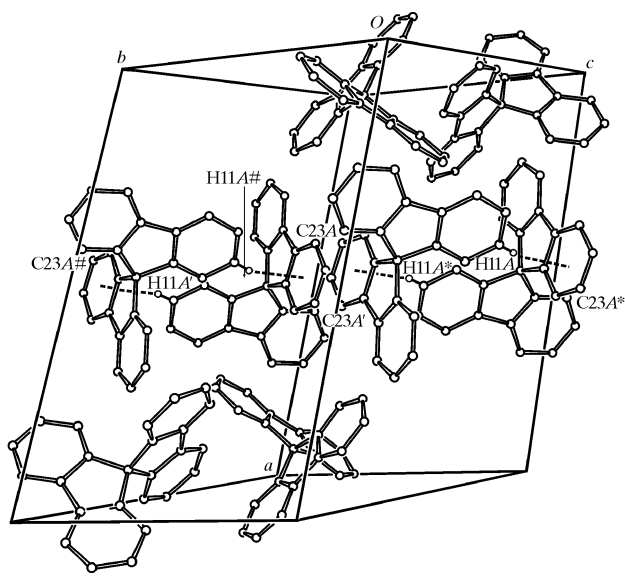
##### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 0.5085P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.111$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
4921 reflections	$\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$
280 parameters	
H-atom parameters constrained	

**Table 1**  
Hydrogen-bond geometry (Å, °) for (I).  
Cg1 is the centroid of the C20–C25 ring.

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
C4–H4...Cg1 <sup>i</sup>	0.95	2.67	3.61	172
C11–H11...C16 <sup>ii</sup>	0.95	2.74	3.6196 (18)	154

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



**Figure 6**  
The hydrogen bonding in (III). Atoms marked with an asterisk (\*), a hash (#) or a prime (') are at the symmetry positions  $(1 - x, -y, 1 - z)$ ,  $(x, 1 + y, z)$  and  $(1 - x, 1 - y, 1 - z)$ , respectively.

## Compound (II)

## Crystal data

$C_{25}H_{16}C_{12}H_{10}$	$Z = 2$
$M_r = 470.58$	$D_x = 1.227 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.774 (4) \text{ \AA}$	Cell parameters from 944 reflections
$b = 11.427 (4) \text{ \AA}$	$\theta = 2.4\text{--}24.2^\circ$
$c = 13.075 (5) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$\alpha = 71.339 (8)^\circ$	$T = 115 (2) \text{ K}$
$\beta = 83.106 (9)^\circ$	Block, colourless
$\gamma = 67.030 (7)^\circ$	$0.14 \times 0.11 \times 0.04 \text{ mm}$
$V = 1273.8 (8) \text{ \AA}^3$	

## Data collection

Bruker SMART CCD area detector diffractometer	4476 independent reflections
$\varphi$ and $\omega$ scans	2416 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$R_{\text{int}} = 0.050$
$T_{\text{min}} = 0.985, T_{\text{max}} = 0.998$	$\theta_{\text{max}} = 25.1^\circ$
6971 measured reflections	$h = -11 \rightarrow 6$
	$k = -13 \rightarrow 13$
	$l = -15 \rightarrow 15$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2)]$
$R[F^2 > 2\sigma(F^2)] = 0.079$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.248$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.92$	$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
4476 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
335 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.022 (6)

Table 2

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ) for (II).

$Cg_2$  is the centroid of the C2–C7 ring and  $Cg_3$  is the centroid of the C8–C13 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C16–H16 $\cdots$ Cg2 <sup>i</sup>	0.95	2.65	3.57	162
C29–H29 $\cdots$ Cg3 <sup>ii</sup>	0.95	2.63	3.56	163
C3–H3 $\cdots$ C27	0.95	2.80	3.692 (5)	157
C28–H28 $\cdots$ C22	0.95	2.84	3.658 (6)	147
C12–H12 $\cdots$ C31 <sup>iii</sup>	0.95	2.87	3.783 (5)	161
C31–H31 $\cdots$ C19 <sup>iv</sup>	0.95	2.80	3.708 (5)	159

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

## Compound (III)

## Crystal data

$C_{25}H_{16}$	$D_x = 1.250 \text{ Mg m}^{-3}$
$M_r = 316.38$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 7135 reflections
$a = 18.2491 (17) \text{ \AA}$	$\theta = 2.2\text{--}25.0^\circ$
$b = 11.1522 (10) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$c = 18.6918 (17) \text{ \AA}$	$T = 115 (2) \text{ K}$
$\beta = 117.907 (2)^\circ$	Block, colourless
$V = 3361.7 (5) \text{ \AA}^3$	$0.30 \times 0.20 \times 0.20 \text{ mm}$
$Z = 8$	

## Data collection

Bruker SMART CCD area-detector diffractometer	5925 independent reflections
$\varphi$ and $\omega$ scans	4923 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$R_{\text{int}} = 0.027$
$T_{\text{min}} = 0.970, T_{\text{max}} = 0.987$	$\theta_{\text{max}} = 25.0^\circ$
18 394 measured reflections	$h = -16 \rightarrow 21$
	$k = -13 \rightarrow 13$
	$l = -22 \rightarrow 18$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.075P)^2 + 0.6111P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.119$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
5925 reflections	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
451 parameters	
H-atom parameters constrained	

H atoms were placed in calculated positions and treated as riding, with C–H distances of 0.95  $\text{\AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Compound (II) contains zero values in the weighting scheme, resulting from weak diffraction by this sample.

For all compounds, data collection: SMART (Bruker, 2000); cell refinement: SAINT-Plus (Bruker, 2000); data reduction: SAINT-Plus; structure solution: SHELXS97 (Sheldrick, 1997); structure refinement: SHELXL97 (Sheldrick, 1997); molecular graphics: CAMERON (Watkin *et al.*, 1996); publication software: SHELXTL (Bruker, 2001).

The authors thank the EPSRC, UK, for funding the purchase of the diffractometer and the University of York for additional financial assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1249). Services for accessing these data are described at the back of the journal.

## References

- Alcazar, V. & Diederich, F. (1992). *Angew. Chem. Int. Ed. Engl.* **31**, 1521–1523.
- Bruker (2000). SMART (Version 5.625), SAINT-Plus (Version 6.22) and SADABS (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2001). SHELXTL. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
- Clarkson, R. G. & Gomberg, M. (1930). *J. Am. Chem. Soc.* **52**, 2881–2896.
- Lowden, L. J. & Chandler, D. (1974). *J. Chem. Phys.* **61**, 5228–5241.
- Poriel, C., Ferrand, Y., le Maux, P., Paul, C., Rault-Berthelot, J. & Simonneaux, G. (2003). *Chem. Commun.* pp. 2308–2309.
- Schenk, H. (1972). *Acta Cryst.* **B28**, 625–628.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Shi, X. Q. & Bartell, L. S. (1988). *J. Phys. Chem.* **92**, 5667–5673.
- Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). CAMERON. Chemical Crystallography Laboratory, University of Oxford, England.
- Williams, J. H. (1993). *Acc. Chem. Res.* **26**, 593–598.
- Wong, K. T., Chien, Y. Y., Chen, R. T., Wang, C. F., Lin, Y. T., Chiang, H. H., Hsieh, P. Y., Wu, C. C., Chou, C. H., Su, Y. O., Lee, G. H. & Peng, S. M. (2002). *J. Am. Chem. Soc.* **124**, 11576–11577.