neutron diffraction for closely related cluster complexes (Lugan, Savariault, Lavigne & Bonnet, 1983, and references cited therein).

Noticeably, each hydride ligand is coplanar, within experimental error, with one face of the metal tetrahedron. The orientations of carbonyl ligands clearly reflect the presence of hydrides.

Finally, all structural features of $Ru_4(\mu\text{-}H)_4(CO)_{10}$-($\mu$-dppm) are analogous to those of $Ru_4(\mu\text{-}H)_4(CO)_{10}$-(diphos). Thus, the different chemical behaviour of the two complexes cannot be related to any structural difference.

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Structure of (2,2-Biphenylylene)(1-pyrrolidinecarbodithioato)iodine(III) Chloroform Solvate

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Abstract. $C_{17}H_{16}INS_2.CHCl_3$, $M_r = 544·7$, triclinic, $P\bar{1}$, $a = 12·082$ (3), $b = 9·859$ (4), $c = 9·638$ (3) Å, $\alpha = 108·46$ (3), $\beta = 108·29$ (3), $\gamma = 89·56$ (3)°, $V = 1028·6$ Å^3, $Z = 2$, $D_m = 1·765$, $D_x = 1·758$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2·15$ mm^{-1}, $F(000) = 536$, $T = 298$ K, final $R = 0·060$ for 1875 independent non-zero reflections. The coordination around each I atom is planar tetragonal comprising two normal bonds to C_{ar} atoms [C—I 2·11 (2), 2·13 (1) Å] and two secondary bonds to S atoms [S···I 3·053 (4), 3·162 (4) Å] of different ligands. Two centrosymmetrically related formula units form a dimer, bis-(2,2′-biphenylylene)-μ-bis(1-pyrrolidinecarbodithioato-*S,S′*)-diiodine(III). Different dimers are held together by van der Waals forces.

Introduction. The structural study of the title compound (BPPI hereafter) is the first of a series of systematic structure determinations of diaryliodinanes with an I—S bond, aiming at a better understanding of bonding in this class of hypervalent iodine compounds. The structures of various classes of hypervalent iodine compounds have revealed interesting features (Koser, 1983), yet none of them refers to an I—S bond. The formation of secondary bonds (Alcock, 1972) is a common characteristic of almost all of these structures.

Experimental. Yellow crystals, 0·40 × 0·22 × 0·20 mm, m.p. 414–415 K. D_m measured by flotation in 1,2-dibromobutane/carbon tetrachloride. Computer-controlled Philips PW 1100 four-circle single-crystal diffractometer. Cell parameters and standard deviations by least-squares analysis of measured θ angles of 80 strong reflections with $\theta = 6–15°$. Three-dimensional data, graphite-monochromated Mo $K\alpha$, ω-scan mode. Intensity statistics indicated $P\bar{1}$. Three standard reflections exhibited same percentage linear decrease in intensity (12%). 2117 measured reflections, $\theta = 3–25°$, index range $h = 0 \rightarrow 13$, $k = -11 \rightarrow 11$, $l = -11 \rightarrow 9$, 1875 with $I > 2\sigma(I)$, $R_{\text{int}} = 0·104$ from merging 586 symmetry-equivalent reflections. Correction for intensity drop, no absorption correction. I atom located by Patterson synthesis, remaining non-H atoms by Fourier synthesis. Full-matrix least squares using F, *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). H atoms at calculated positions (C—H 1·1 Å) with

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isotropic temperature factors as those of bonded C atoms, not refined. $w = (F_o/60)^2$ for $F_o \leq 60$, $w = (60/F_o)^2$ for $F_o > 60$. $R = 0{\cdot}060$, $wR = 0{\cdot}055$, $S = 1{\cdot}79$, $(\Delta/\sigma)_{\max} = 0{\cdot}22$, $(\Delta/\sigma)_{\text{mean}} = 0{\cdot}03$, $\Delta\rho = -0{\cdot}86$ to $0{\cdot}80$ e Å^{-3} in region of I atom. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final positional parameters and equivalent isotropic temperature coefficients for the non-H atoms are given in Table 1.* Interatomic distances and angles are in Table 2. A clinographic projection of the BPPI dimer is shown in Fig. 1. Two covalent I—C_{ar} bonds and two secondary I···S bonds to two centrosymmetrically related dithiocarbamate (dtc) ligands form a planar tetragonal coordination around the I atom [angles: 94·5 (1), 91·9 (3), 91·1 (4), 81·9 (5)° (see Table 2); max. deviation from mean plane 0·109 (8) Å]. The two bond lengths I(1)—C(6) = 2·13 (1) and I(1)—C(12) = 2·11 (2) Å are comparable with the sum of the covalent radii, 2·05 Å (Pauling, 1960). The I(1)···S(1) = 3·053 (4) and I(1)···S(2^{i}) = 3·162 (4) Å bonds are longer than the sum of the covalent radii, 2·37 Å, but significantly shorter than the sum of the van der Waals radii, 3·78 Å (Bondi, 1964), and may be considered as secondary bonds (Alcock, 1972). I(1)···S(2) = 3·893 (4) Å is longer than the van der Waals distance. The (diphenyleno)iodonium (DPI) group and the S(1) and S(2^{i}) atoms form an almost planar system with maximum distance from the mean plane 0·21 (1) Å [S(2^{i})]. The dtc ligand is planar to

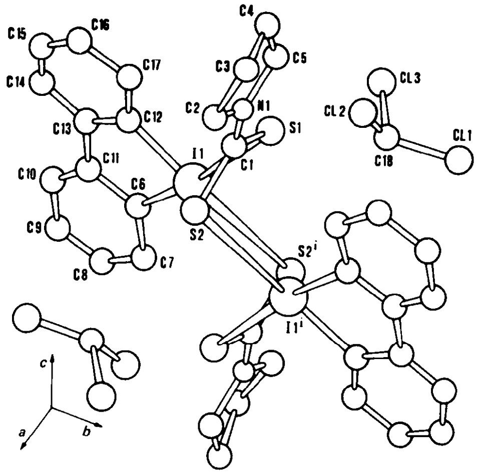

Fig. 1. Clinographic projection of the BPPI dimer.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

	x	y	z	B_{eq}*
I(1)	0·3911 (1)	0·3320 (1)	0·0181 (1)	2·9
S(1)	0·5307 (3)	0·5802 (4)	0·3047 (5)	3·9
S(2)	0·7231 (3)	0·4675 (4)	0·1761 (4)	3·8
C(1)	0·674 (1)	0·547 (1)	0·330 (2)	3·0
N(1)	0·749 (1)	0·592 (1)	0·471 (1)	3·6
C(2)	0·876 (1)	0·577 (2)	0·513 (2)	4·3
C(3)	0·925 (2)	0·677 (3)	0·677 (2)	7·3
C(4)	0·831 (2)	0·688 (2)	0·746 (2)	5·1
C(5)	0·719 (1)	0·665 (2)	0·616 (2)	4·1
C(6)	0·288 (1)	0·147 (1)	−0·162 (2)	3·0
C(7)	0·221 (1)	0·142 (2)	−0·303 (2)	3·8
C(8)	0·159 (1)	0·012 (2)	−0·409 (2)	4·2
C(9)	0·164 (1)	−0·111 (2)	−0·364 (2)	4·4
C(10)	0·229 (1)	−0·100 (2)	−0·217 (2)	4·1
C(11)	0·297 (1)	0·028 (2)	−0·109 (2)	3·0
C(12)	0·436 (1)	0·183 (1)	0·137 (2)	2·9
C(13)	0·375 (1)	0·045 (2)	0·047 (2)	3·3
C(14)	0·395 (1)	−0·062 (1)	0·115 (2)	3·8
C(15)	0·474 (1)	−0·032 (2)	0·263 (2)	4·2
C(16)	0·534 (1)	0·103 (2)	0·348 (2)	3·6
C(17)	0·516 (1)	0·214 (1)	0·286 (2)	3·5
C(18)	0·102 (2)	0·712 (2)	0·113 (2)	6·7
Cl(1)	0·0895 (6)	0·8879 (6)	0·1157 (8)	9·7
Cl(2)	0·2369 (5)	0·6960 (6)	0·2372 (7)	8·3
Cl(3)	−0·0123 (4)	0·6565 (6)	0·1650 (7)	7·7

* $B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

Table 2. *Interatomic distances* (Å) *and angles* (°)

I(1)···S(1)	3·053 (4)	C(9)—C(10)	1·36 (2)
I(1)···S(2^{i})	3·162 (4)	C(10)—C(11)	1·41 (2)
I(1)···S(2)	3·893 (4)	C(11)—C(6)	1·41 (2)
I(1)—C(6)	2·13 (1)	C(11)—C(13)	1·46 (2)
I(1)—C(12)	2·11 (2)	C(12)—C(13)	1·42 (2)
C(1)—S(1)	1·71 (1)	C(13)—C(14)	1·39 (2)
C(1)—S(2)	1·72 (2)	C(14)—C(15)	1·39 (2)
C(1)—N(1)	1·31 (2)	C(15)—C(16)	1·38 (2)
N(1)—C(2)	1·48 (2)	C(16)—C(17)	1·40 (3)
C(2)—C(3)	1·50 (2)	C(17)—C(12)	1·39 (2)
C(3)—C(4)	1·47 (3)	C(18)—Cl(1)	1·73 (2)
C(4)—C(5)	1·50 (2)	C(18)—Cl(2)	1·73 (2)
C(5)—N(1)	1·51 (2)	C(18)—Cl(3)	1·76 (2)
C(6)—C(7)	1·34 (2)	S(2)···H(C7^{i})	2·77
C(7)—C(8)	1·39 (2)	S(2)···H(C10^{ii})	2·76
C(8)—C(9)	1·41 (3)	N(1)···H(C7^{i})	2·50

S(1)···I(1)···S(2)	94·5 (1)	C(7)—C(6)—C(11)	123·3 (11)
S(1)···I(1)···S(2)	49·6 (1)	C(6)—C(7)—C(8)	119·4 (16)
S(1)···I(1)—C(6)	172·5 (5)	C(7)—C(8)—C(9)	120·1 (15)
S(1)···I(1)—C(12)	91·9 (9) (3)	C(8)—C(9)—C(10)	118·4 (13)
S(2^{i})···I(1)—C(6)	91·1 (4)	C(9)—C(10)—C(11)	122·8 (17)
S(2^{i})···I(1)—C(12)	169·8 (4)	C(10)—C(11)—C(6)	115·7 (13)
C(6)—I(1)—C(12)	81·9 (5)	C(10)—C(11)—C(13)	125·7 (15)
I(1)···S(1)—C(1)	104·2 (4)	C(6)—C(11)—C(13)	118·5 (11)
I(1)···S(2)—C(1)	96·1 (5)	I(1)—C(12)—C(13)	111·8 (10)
S(1)—C(1)—S(2)	122·4 (8)	I(1)—C(12)—C(17)	124·6 (10)
S(1)—C(1)—N(1)	118·2 (12)	C(13)—C(12)—C(17)	123·5 (15)
S(2)—C(1)—N(1)	119·3 (12)	C(12)—C(13)—C(11)	117·0 (15)
C(1)—N(1)—C(2)	125·5 (14)	C(12)—C(13)—C(14)	117·2 (12)
C(1)—N(1)—C(5)	125·1 (13)	C(11)—C(13)—C(14)	125·8 (12)
C(2)—N(1)—C(5)	109·4 (11)	C(13)—C(14)—C(15)	120·1 (13)
N(1)—C(2)—C(3)	103·7 (13)	C(14)—C(15)—C(16)	121·8 (17)
C(2)—C(3)—C(4)	107·5 (14)	C(15)—C(16)—C(17)	120·3 (13)
C(3)—C(4)—C(5)	106·0 (15)	C(16)—C(17)—C(12)	117·1 (12)
C(4)—C(5)—N(1)	105·1 (13)	Cl(1)—C(18)—Cl(2)	111·4 (9)
I(1)—C(6)—C(7)	126·1 (11)	Cl(1)—C(18)—Cl(3)	108·7 (11)
I(1)—C(6)—C(11)	110·5 (9)	Cl(2)—C(18)—Cl(3)	110·6 (13)

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

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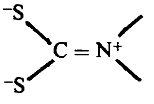
* Lists of structure amplitudes, anisotropic thermal parameters, coordinates and isotropic temperature factors for H atoms and least-squares-planes calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42839 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

within 0·021 (9) Å and the mean plane is nearly perpendicular to the DPI–S(1)–$S(2^{i})$ plane [dihedral angle 99·8 (3)°]. A chair-shaped pseudo-ring is formed by I(1), S(1), C(1), S(2) and their centrosymmetric equivalents; thus two formula units form a dimer around an inversion center.

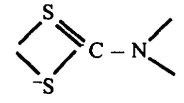
The coordination around the I atom with two normal and two secondary bonds agrees well with those of the diaryliodonium salt structures studied so far, *i.e.* diphenyliodonium nitrate (Wright & Meyers, 1972), dibenziodolium tetrafluoroborate (Beringer, Ganis, Avitabile & Jaffe, 1972; Struchkov & Khotsyanova, 1960), diphenyliodonium iodide (Khotsyanova & Struchkov, 1952*a*) and diphenyliodonium chloride (Khotsyanova & Struchkov, 1952*b*), $(C_6H_5)_2IX$ (X = Cl, Br or I) (Alcock & Countryman, 1977), but not with that of bis(*p*-methoxyphenyl)(*N,N*-diethyldithiocarbamato)iodine (Bozopoulos & Rentzeperis, 1986).

The dtc ligand is bidentate. The angles I(1)···S(1)–C(1) and $I(I^{i})$···S(2)–C(1) are 104·2 (4) and 96·1 (5)° respectively. The S–C(N) bond lengths, 1·71 (1) and 1·72 (2) Å, compare well with values found in other dtc ligands (Coucouvanis, 1970, 1979).

The C(1)–N(1) distance implies strong double-bond character. The contributions of the resonance structures usually assumed for the dtc ligands, calculated according to valence-bond theory (Pauling, 1960), are 65% for (I) and 35% for (II). This study once more confirms that (I) makes a major contribution to the structure of dithiocarbamates.



(I)



(II)

The pyrrolidine ring is puckered as expected and compares well with the rings found in tris(1-pyrrolidinecarbodithioato)antimony(III) (Kavounis, Kokkou, Rentzeperis & Karagiannidis, 1980). Maximum deviations of two adjacent atoms, C(3) and C(4), from the plane of the remaining three atoms are −0·38 (5) and 0·05 (5) Å respectively.* Since C(4) lies almost on the plane, the conformation of the ring is of the envelope type.

Fig. 2 is a clinographic projection of the structure showing the molecular packing. Selected intermolecular distances are shown in Table 2.

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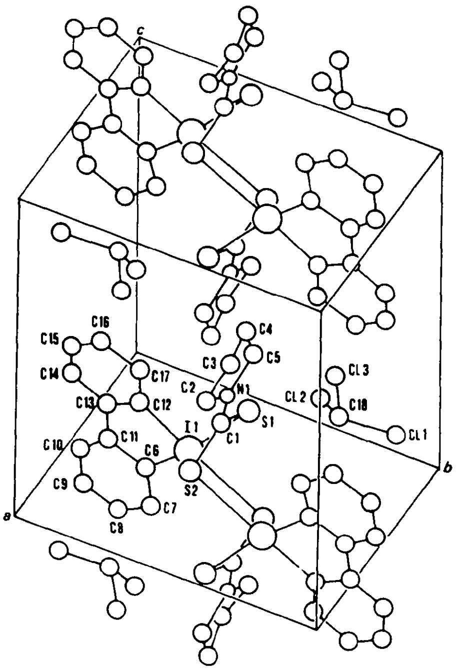

Fig. 2. Clinographic projection of BPPI showing the molecular packing in the unit cell.

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* See deposition footnote.