interatomic distances range from 0·85 to 1·21 Å with an average of 0·98 Å and an average standard deviation of about 0·06 Å. Intermolecular contacts are reasonable and give no indication of hydrogen bonding.

The bond angles and distances are similar in several respects to those in 5α-bromo-8β,9α-dimethylhydrindane-1,4-dione (Yordy & Neuman, 1974). The major structural differences between this molecule and the title compound are [all atom numbers are those of the present study]: the bromine replacing H(3); the carbonyl oxygen replacing both H(1) and the methoxy group at C(2); and two hydrogens replacing the group at C(8).

Of particular interest is the bond C(1)–C(6), which is shared by the two rings, and the geometries around C(1) and C(6). This bond length is 1·553 (5) Å in the present study, compared with 1·61 (2) Å in the compound reported by Yordy & Neuman (1974). The average difference between the two molecules in the angles around C(1) is 3·5 and around C(6) is 3·3°. The angle C(1)–C(6)–C(12) is 8·3° larger in the present study; this difference is probably due to the steric interaction between the methyl C(12) and the methoxy group. The angle C(6)–C(1)–C(9) is 8·2° smaller in the present study; this difference is probably due to the extra strain in the five-membered ring when it has two adjacent double bonds to it. The significant differences between the bond angles and distances in the two compounds appear to be due to the steric and bond-strain effects of the differences in the chemical structures.

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Di-μ-iodo-bis[diiodobis(triphenylphosphine oxide)bismuth(III)]

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Abstract. $\{BiI_3[(C_6H_5)_3PO]_2\}_2$, monoclinic, $P2_1/n$ (alternative setting for $P2_1/c$, No. 14); $a=12{\cdot}899$ (5), $b=11{\cdot}778$ (1), $c=25{\cdot}212$ (3) Å, $\beta=102{\cdot}95$ (9)°; $D_o=2{\cdot}01$ (1) g cm^{-3}, $Z=2$, $D_c=2{\cdot}039$ g cm^{-3}; $R=0{\cdot}033$ for 4331 reflexions [$I>1{\cdot}5\sigma(I)$]. The structure consists of binuclear complex molecules with two distorted octahedra sharing an edge. Each of the Bi atoms is coordinated with two organic ligands, and two terminal and two bridging iodine atoms, arranged in *cis* positions.

Introduction. A series of coordination compounds was prepared in the systems Sb or Bi trihalide–triphenylphosphine oxide and triphenylarsine oxide and characterized using vibrational spectra (Milićev & Hadži, 1971, 1976). In order to establish the complete structures of these compounds crystal structure analysis was undertaken. As the first example the crystal structure of triiodobismuth(III)-tri-μ-iodotris(triphenylarsine oxide)bismuth(III), $I_3BiI_3Bi[(C_6H_5)_3AsO]_3$, was reported (Lazarini, Golič & Pelizzi, 1975, 1976). The structure of the title compound, obtained under similar conditions, is different.

The unit-cell parameters were calculated by a least-squares method from Al-calibrated Weissenberg photographs (Cu $K\alpha_1$, $\lambda=1{\cdot}54051$ Å, $T=20$ °C). The intensity data were collected using an Enraf–Nonius CAD-4 diffractometer with the ω–2θ scan and Mo $K\alpha$ radiation (graphite monochromator, $\lambda=0{\cdot}7107$ Å). A set of 6566 independent reflexions within the θ range 1·5–25° was recorded, and of these 4331 reflexions, having $I>1{\cdot}5\sigma(I)$ (calculations based on counting statistics), were used in the structure analysis. The intensities were corrected for Lorentz and polarization effects. Absorption correction was not applied (μMo $K\alpha=71{\cdot}2$ cm^{-1}, approximate dimensions of the crystal $0{\cdot}20\times0{\cdot}20\times0{\cdot}15$ mm; $\mu r\simeq0{\cdot}7$).

The positions of one Bi and three I atoms were determined from the three-dimensional Patterson function. The remaining non-hydrogen atoms were located using two successive Fourier summations. The structure was then refined by least-squares with anisotropic thermal parameters for Bi, I, P and O atoms, isotropic thermal parameters for C atoms and with anomalous dispersion correction for Bi, I and P. The function minimized in the least-squares procedure was $\sum w(|F_o|-|F_c|)^2$. The weighting scheme applied was as follows:

$F_o < 50$:
$w_F = (F_o/50)^{1\cdot0}$; $\sin\theta < 0\cdot20$; $w_s = (\sin\theta/0\cdot20)^{1\cdot5}$

$50 < F_o \le 125$:
$w_F = 1\cdot0$; $0\cdot20 < \sin\theta \le 0\cdot35$; $w_s = 1\cdot0$

$F_o > 125$:
$w_F = (125/F_o)^{1\cdot5}$; $\sin\theta > 0\cdot35$; $w_s = (0\cdot35/\sin\theta)^{1\cdot7}$

$$w = 0\cdot5 w_F w_s\,.$$

The H parameters were calculated and included in the structure factor calculation (with an isotropic temperature factor $U = 0\cdot05$ Å^2) but not refined. Final R values are $R = \sum||F_o|-|F_c||/\sum|F_o| = 0\cdot033$ and $R_w = [\sum w(F_o-F_c)^2/\sum wF_o^2]^{1/2} = 0\cdot038$ for 4331 reflexions and 217 parameters. The average parameter shift to error ratio was 0·88 in the final cycle.

All calculations were performed on the CDC Cyber 72 computer of RRC Ljubljana using the X-RAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) adapted by Professor L. Golič. Atomic scattering factors tabulated by Cromer & Mann (1968) for the heavy atoms and those tabulated by Stewart, Davidson & Simpson (1965) for H atoms were used. The values of $\Delta f'$ and $\Delta f''$ for anomalous dispersion correction tabulated by Cromer (1965) were applied.

The positional and thermal parameters (with standard deviations in parentheses) of the non-carbon atoms are listed in Table 1 and those of the carbon atoms in Table 2. The structure of the complex molecule and the atom numbering system used are shown in Fig. 1. The important interatomic distances and angles (with standard deviations in parentheses) are given in Table 3.*

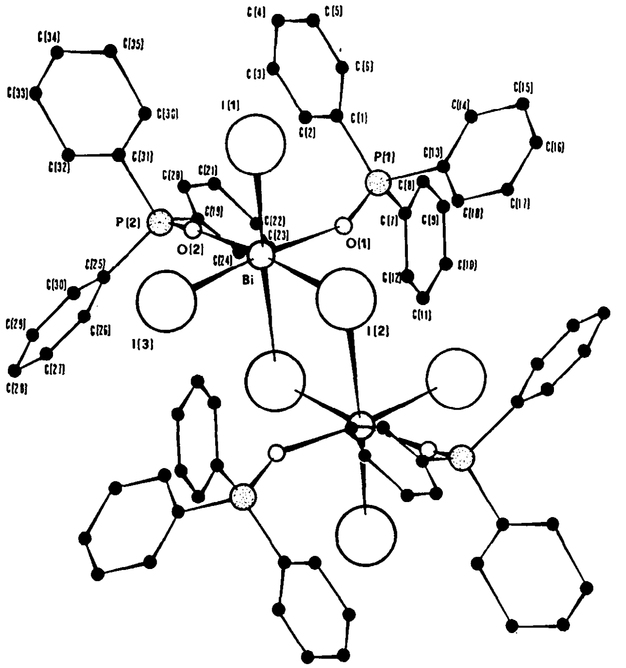

Fig. 1. The molecule of $\{BiI_3[(C_6H_5)_3PO]_2\}_2$ projected along the b axis.

Discussion. The binuclear complexes of BiI_3 with triphenylarsine oxide and triphenylphosphine oxide are built differently. The structure of $I_3BiI_3Bi[(C_6H_5)_3AsO]_3$ consists of molecules with two distorted octahedra sharing a face through I atoms and with all of the triphenylarsine oxide ligands linked to one of the Bi atoms (Lazarini, Golič & Pelizzi, 1975, 1976). In contrast, the symmetrical molecules of the title compound are built of two octahedra sharing an edge through I atoms and with triphenylphosphine oxide ligands in *cis* positions. The three types of Bi–I distances of the title compound [Bi–I(terminal) 2·901 (2) and 2·947 (1) Å, Bi–I(bridging) opposite to the organic ligand 3·050 (1) Å, and Bi–I(bridging) opposite to the ter-

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31843 (20 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final positional parameters* ($\times 10^5$) *and thermal parameters* ($\times 10^4$) *for non-carbon atoms*

The anisotropic temperature factor is in the form:

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	52068 (3)	51546 (3)	41320 (1)	341 (2)	307 (2)	290 (2)	7 (1)	114 (1)	18 (1)
I(1)	44742 (5)	41946 (6)	30534 (3)	534 (4)	452 (4)	391 (3)	−36 (3)	51 (3)	−58 (3)
I(2)	40541 (5)	34234 (5)	46917 (2)	553 (4)	385 (3)	401 (3)	−72 (3)	188 (3)	13 (3)
I(3)	71981 (5)	38347 (6)	43599 (3)	477 (4)	554 (4)	538 (4)	152 (3)	169 (3)	94 (3)
P(1)	26754 (18)	70255 (20)	36629 (9)	341 (12)	394 (13)	342 (12)	47 (10)	81 (10)	25 (10)
P(2)	66588 (18)	76935 (20)	36193 (9)	376 (12)	338 (12)	386 (12)	−42 (10)	154 (10)	27 (10)
O(1)	36251 (49)	64107 (59)	39982 (26)	347 (34)	561 (42)	452 (37)	69 (30)	48 (29)	61 (32)
O(2)	60856 (51)	67014 (55)	37927 (26)	434 (37)	431 (37)	485 (37)	−71 (30)	194 (30)	57 (30)

Table 2. *Final positional parameters* (× 10^4) *and thermal parameters* (× 10^3) *for carbon atoms*

The isotropic temperature factor is in the form: $\exp[-8\pi^2U(\sin\theta/\lambda)^2]$.

	x	*y*	*z*	*U*
C(1)	2822 (7)	7343 (8)	2986 (4)	35 (2)
C(2)	3408 (8)	8278 (8)	2890 (4)	44 (2)
C(3)	3622 (8)	8444 (9)	2375 (4)	46 (2)
C(4)	3227 (9)	7690 (10)	1963 (4)	53 (3)
C(5)	2636 (8)	6752 (9)	2052 (4)	50 (2)
C(6)	2441 (8)	6579 (8)	2563 (4)	43 (2)
C(7)	2478 (7)	8356 (8)	3987 (4)	37 (2)
C(8)	1854 (8)	9225 (9)	3713 (4)	47 (2)
C(9)	1692 (9)	10199 (10)	3999 (5)	60 (3)
C(10)	2148 (11)	10285 (11)	4554 (5)	68 (3)
C(11)	2729 (9)	9420 (11)	4823 (5)	59 (3)
C(12)	2920 (8)	8439 (9)	4548 (4)	47 (2)
C(13)	1467 (7)	6218 (8)	3603 (4)	38 (2)
C(14)	521 (8)	6521 (9)	3248 (4)	51 (2)
C(15)	−401 (9)	5869 (10)	3225 (5)	64 (3)
C(16)	−357 (10)	4954 (11)	3553 (5)	69 (3)
C(17)	572 (10)	4647 (11)	3916 (5)	70 (3)
C(18)	1498 (8)	5280 (9)	3940 (4)	52 (2)
C(19)	5946 (7)	9004 (7)	3645 (3)	36 (2)
C(20)	5932 (8)	9870 (9)	3275 (4)	49 (2)
C(21)	5438 (9)	10895 (9)	3338 (4)	58 (3)
C(22)	4937 (8)	11036 (9)	3768 (4)	54 (2)
C(23)	4939 (7)	10151 (8)	4127 (4)	53 (2)
C(24)	5404 (6)	9134 (7)	4073 (3)	43 (2)
C(25)	7970 (7)	7888 (8)	4049 (4)	43 (2)
C(26)	8480 (9)	6945 (9)	4323 (4)	56 (3)
C(27)	9525 (10)	7070 (12)	4634 (5)	72 (3)
C(28)	10008 (11)	8118 (12)	4677 (5)	76 (3)
C(29)	9495 (11)	9043 (12)	4424 (6)	76 (4)
C(30)	8462 (9)	8926 (10)	4104 (5)	60 (3)
C(31)	6814 (6)	7502 (7)	2932 (3)	37 (2)
C(32)	7566 (8)	8099 (9)	2729 (4)	54 (2)
C(33)	7632 (9)	7913 (10)	2180 (5)	64 (3)
C(34)	6976 (9)	7160 (11)	1863 (5)	68 (3)
C(35)	6223 (11)	6548 (12)	2072 (5)	74 (3)
C(36)	6140 (9)	6731 (10)	2610 (4)	58 (3)

Table 3. *Interatomic distances* (Å) *and angles* (°)

The weighted mean distances and angles ($\bar{X}$) and the average standard deviations $\sigma(\bar{X})$ were calculated as:

$$\bar{X}=\sum_i (X_i/\sigma_i^2)/\sum_i \sigma_i^{-2}, \quad \sigma(\bar{X})=1/\sum_i \sigma_i^{-2}.$$

Bi–I(1)	2·901 (2)	O(1)–P(1)	1·508 (6)
Bi–I(3)	2·947 (1)	O(2)–P(2)	1·499 (7)
Bi–I(2)	3·050 (1)	P(1)–C(1)	1·80 (1)
Bi–I(2)$^{\mathrm{i}}$	3·353 (2)	P(1)–C(7)	1·81 (1)
Bi–O(1)	2·481 (6)	P(1)–C(13)	1·80 (1)
Bi–O(2)	2·402 (7)	P(2)–C(19)	1·805 (9)
Bi–Bi$^{\mathrm{i}}$	4·541 (1)	P(2)–C(25)	1·807 (9)
		P(2)–C(31)	1·801 (9)

C–C (mean)	1·388 (2)
C–C (max.)	1·42 (2)
C–C (min.)	1·35 (2)

I(1)—Bi–I(2)	94·76 (2)	Bi—I(2)—Bi$^{\mathrm{i}}$	90·22 (2)
I(1)—Bi–I(3)	93·66 (2)	Bi—O(1)–P(1)	154·4 (4)
I(1)—Bi–O(1)	91·1 (1)	Bi—O(2)–P(2)	176·2 (4)
I(1)—Bi–O(2)	92·4 (2)	O(1)—P(1)–C(1)	112·7 (4)
I(1)—Bi–I(2)$^{\mathrm{i}}$	172·84 (2)	O(1)—P(1)–C(7)	109·9 (4)
I(2)$^{\mathrm{i}}$–Bi–I(2)	89·78 (2)	O(1)—P(1)–C(13)	111·8 (4)
I(2)$^{\mathrm{i}}$–Bi–I(3)	91·63 (2)	C(1)—P(1)–C(7)	107·6 (4)
I(2)$^{\mathrm{i}}$–Bi–O(1)	83·4 (1)	C(1)—P(1)–C(13)	107·6 (4)
I(2)$^{\mathrm{i}}$–Bi–O(2)	82·7 (2)	C(7)—P(1)–C(13)	106·7 (4)
I(2)—Bi–I(3)	92·93 (3)	O(2)—P(2)–C(19)	111·6 (4)
I(2)—Bi–O(1)	89·4 (2)	O(2)—P(2)–C(25)	112·4 (4)
I(2)—Bi–O(2)	171·8 (2)	O(2)—P(2)–C(31)	110·6 (4)
I(3)—Bi–O(1)	174·5 (1)	C(19)–P(2)–C(25)	106·6 (4)
I(3)—Bi–O(2)	90·5 (2)	C(19)–P(2)–C(31)	108·0 (4)
O(1)–Bi–O(2)	86·5 (2)	C(25)–P(2)–C(31)	107·5 (4)

C–C–C (mean)	119·9 (2)	P–C–C (mean)	119·8 (2)
C–C–C (max.)	122 (1)	P–C–C (max.)	122·6 (7)
C–C–C (min.)	118·4 (8)	P–C–C (min.)	116·6 (7)

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

minal iodine 3·353 (2) Å] are comparable with those found in the triphenylarsine oxide compound [mean distances 2·934 (1), 3·151 (1) and 3·325 (1) Å]. The Bi–O distances [2·402 (7) and 2·481 (6) Å] are significantly longer than in the triphenylarsine oxide complex [mean distance 2·268 (8) Å], which is in agreement with the already established relative Lewis basicity of these two oxo-bases (Hadži, Klofutar & Oblak, 1968; Milićev & Hadži, 1976). The P–O distances [1·499 (7) and 1·508 (6) Å] are somewhat longer than in free triphenylphosphine oxide [1·46 (1) Å] (Bandoli, Bortolozzo, Clemente, Croatto & Panattoni, 1970). A considerable *trans* influence of the ligands is present. Significant intermolecular contacts were not observed.

An analogous compound of BiBr$_3$ with triphenylphosphine oxide is isomorphous with the title compound, judging from powder diffraction data (Milićev & Hadži, 1976).

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