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 5x-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.

We thank the National Institutes of Health for support of the synthesis of the title compound (Grant 2 RO1 AM 10849-08) and Dr William H. Reusch for his helpful discussions.

References

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

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(Received 5 April 1976; accepted 27 April 1976)

Abstract. {Bi4[(C6H5)3PO]2}2, monoclinic, P21/c (alternative setting for P21/n, No. 14); a=12.899 (5), b=11.778 (1), c=25.212 (3) Å, β=102.95 (9)°; Dc=2.01 (1) g cm−3, Z=2, Dc=2.039 g cm−3; R=0.033 for 4331 reflexions [I>1.5σ(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 (Miličev & 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), I3Bi3Bi[(C6H5)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 Kα1, λ=1.54051 Å, T=20°C). The intensity data were collected using an Enraf–Nonius CAD-4 diffractometer with the ω-2θ scan and Mo Kα radiation (graphite monochromator, λ=0.7107 Å). A set of 6566 independent reflexions within the θ range 1.5–25° was recorded, and of these 4331 reflexions, having I>1.5σ(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 Kα=71.2 cm−1, approximate dimensions of the crystal 0.20×0.20×0.15 mm; μn=0.7).

The positions of one Bi and three I atoms were deter-
mined 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, 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:

$$
F_o < 50: \quad w_p = (F_o/50)^{1.0}; \quad \sin \theta < 0.20; \quad w_s = (\sin \theta/0.20)^{1.5}
$$

$$
50 < F_o \leq 125: \quad w_p = 1.0; \quad 0.20 < \sin \theta \leq 0.35; \quad w_s = 1.0
$$

$$
F_o > 125: \quad w_p = (125/F_o)^{1.5}; \quad \sin \theta > 0.35; \quad w_s = (0.35/\sin \theta)^{1.7}
$$

$$
w = 0.5w_pw_s.
$$

Discussion. The binuclear complexes of Bi$_3$ with triphenylarsine oxide and triphenylphosphine oxide are built differently. The structure of I$_2$Bi$_3$Bi$_2$[(C$_6$H$_5$)$_3$AsO$_2$]$_2$, consisting 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, Golić & 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(biracing) opposite to the organic ligand 3.050 (1) Å, and Bi–I(biracing) opposite to the termi-

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

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U$_{11}$</th>
<th>U$_{22}$</th>
<th>U$_{33}$</th>
<th>U$_{12}$</th>
<th>U$_{13}$</th>
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<td>Bi</td>
<td>52068 (3)</td>
<td>51546 (3)</td>
<td>41320 (1)</td>
<td>341 (2)</td>
<td>307 (2)</td>
<td>290 (2)</td>
<td>7 (1)</td>
<td>114 (1)</td>
<td>18 (1)</td>
</tr>
<tr>
<td>I(1)</td>
<td>44742 (5)</td>
<td>41946 (6)</td>
<td>30534 (3)</td>
<td>534 (4)</td>
<td>452 (4)</td>
<td>391 (3)</td>
<td>-36 (3)</td>
<td>51 (3)</td>
<td>-58 (3)</td>
</tr>
<tr>
<td>I(2)</td>
<td>40541 (5)</td>
<td>34234 (5)</td>
<td>46917 (2)</td>
<td>553 (4)</td>
<td>385 (3)</td>
<td>401 (3)</td>
<td>-72 (3)</td>
<td>188 (3)</td>
<td>13 (3)</td>
</tr>
<tr>
<td>I(3)</td>
<td>71981 (5)</td>
<td>38347 (6)</td>
<td>43599 (3)</td>
<td>477 (4)</td>
<td>554 (4)</td>
<td>534 (3)</td>
<td>152 (3)</td>
<td>169 (3)</td>
<td>94 (3)</td>
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<tr>
<td>P(1)</td>
<td>26754 (18)</td>
<td>70255 (20)</td>
<td>36629 (9)</td>
<td>341 (12)</td>
<td>394 (13)</td>
<td>342 (12)</td>
<td>47 (10)</td>
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<tr>
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<td>76935 (20)</td>
<td>36193 (9)</td>
<td>376 (12)</td>
<td>338 (12)</td>
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<td>64107 (59)</td>
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<td>485 (37)</td>
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<td>194 (30)</td>
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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 o xo-bases (Hadži, Klofutar & Oblak, 1968; Milčev & 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 BiBr₃ with triphenylphosphine oxide is isomorphous with the title compound, judging from powder diffraction data (Milčev & Hadži, 1976).

The authors wish to thank Professor L. Golić for his interest in this investigation and for many helpful discussions. The financial assistance of the Boris Kidrič Fund is also acknowledged.

References