# Secondary Bonding. Part 5.[1] The Crystal and Molecular Structures of Phenyliodine(III) Diacetate and Bis(dichloroacetate)

By **Nathaniel W. Alcock,* Rachel M. Countryman, Steinar Esperås, and Jeffery F. Sawyer,** Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

The crystal structures of the title compounds (1) and (2) respectively have been determined at −60 °C from diffractometer data by the heavy-atom method. Crystals of (1) are orthorhombic, space group *Pnn*2, with unit-cell dimensions $a$ = 15.693(3), $b$ = 8.477(2), $c$ = 8.762(2) Å, $Z$ = 4, and $R$ = 0.021 for 1 063 observed reflections. Crystals of (2) are triclinic, space group $P\bar{1}$, with $a$ = 10.462(3), $b$ = 4.870(2), $c$ = 15.445(5) Å, $\alpha$ = 101.03(3), $\beta$ = 99.89(3), $\gamma$ = 94.40(3)°, $Z$ = 2, and $R$ = 0.058 for 1 580 observed reflections. For (1) the results are in good agreement with a recent independent determination. In both (1) and (2) the iodine(III) atoms form three covalent bonds with distorted T-shaped geometry. The I–C distances in both compounds are the same (2.08—2.09 Å). The two I–O distances are the same (av. 2.156 Å) for (1) but differ significantly for (2) [2.136(6) and 2.163(7) Å]. The *overall* geometry of each iodine, however, can be described as a pentagonal-planar arrangement of three strong and two weak secondary bonds. In (1) both of these secondary I–O bonds are intramolecular. In (2), however, one of the ligands is unidentate, the other unsymmetrically bidentate, forming inter- and intra-molecular I · · · O contacts to give a dimeric arrangement. The formation and nature of the secondary bonds in (1) and (2) is discussed and compared with other pentagonal-planar systems. A possible orbital-overlap scheme is proposed to explain this geometry.

BEFORE 1970, crystallographic studies of compounds containing organoiodine(III) were restricted to phenyliodine(III) dichloride ($IPhCl_2$) [2] and the diphenyl derivatives.[3] However, recently, many more structures containing this oxidation state of iodine have been published.[4-6] In particular, complexes containing the benziodoxoline heterocyclic ring have been investigated by Gougoutas and others, in order to understand the solid-state topotactic transformations displayed by these compounds.[7] In almost all of these compounds the iodine(III) atoms form three covalent bonds to other atoms in slightly distorted T-shaped geometry, as expected for five electron pairs. As well as covalent bonds, virtually all of the known structures also contain weak inter- and intra-molecular co-ordination bonds of remarkably constant orientation around the iodine atoms. The lengths of these co-ordination interactions are less than the sum of the van der Waals radii for the atoms concerned, and can be described as secondary bonds.[8]

To investigate these features of iodine(III) co-ordination geometries, the crystal structures of the title compounds were determined at −60 °C, thus avoiding the rapid decomposition of the crystals by $X$-ray radiation at room temperature. This forms part of a systematic study of secondary bonding in non-metal complexes and of the effect which attached groups have on the secondary bond strengths. After the completion of this work, the structure of (1) was reported independently,[9] without discussion of the I–O interaction.

## EXPERIMENTAL

Phenyliodine(III) diacetate and phenyliodine(III) bis(dichloroacetate) were prepared by treating iodosylbenzene with the appropriate acid.[10] The diacetate can be recrystallised from benzene, the bis(dichloroacetate) from carbon tetrachloride or ethanol.

(*a*) *Phenyliodine*(III) *Diacetate* (1).—For the data collection, the crystal used was obtained by cleaving a long thick needle perpendicular to the needle axis. At room temperature the crystals rapidly decompose in the $X$-ray beam. However, by cooling the crystal to −60 °C, using a Syntex LT-1 attachment, the problem of crystal decomposition was solved. Curiously, the independent study of (1) did not report any decomposition.

*Crystal data.* $C_{10}H_{11}IO_4$, Orthorhombic, $a$ = 15.693(3), $b$ = 8.477(2), $c$ = 8.762(2) Å, $U$ = 1 165.5(5) Å$^3$, $Z$ = 4, $D_c$ = 1.835 g cm$^{-3}$, Mo-$K_\alpha$ radiation, $\lambda$ = 0.710 69 Å, $\mu$(Mo-$K_\alpha$) = 27.75 cm$^{-1}$, $F$(000) = 624.0, −60 °C. Systematic absences $0kl$ with $k + l \neq 2n$ and $h0l$ with $h + l \neq 2n$ indicate space groups *Pnnm* (no. 58) or *Pnn*2 (no. 34).

Unit-cell dimensions and data were collected using a Syntex $P2_1$ diffractometer. Reflections were measured using $\theta$—$2\theta$ scans over a scan range ($K_{\alpha_1}$ −1.0°) to ($K_{\alpha_2}$ +1.0°) to a maximum 2θ of 51°. A variable scan rate of 1—29.3° min$^{-1}$, depending on the intensity of a preliminary 2-s count, was used. Background counts were recorded at each end of the scan, each for one quarter of the scan time. The intensities of three standard reflections were monitored every 55 reflections. These reflections showed no significant loss in intensity. 1 306 Data were collected, of which 1 063 were considered observed [$I/\sigma(I) \geqslant 3.0$] and used in refinement. Two reflections (002 and 020) were too intense to be measured accurately and were discarded. Lorentz, polarisation, and absorption corrections were applied, the last with the program ABSCOR.[11]

A Patterson synthesis revealed the position of a single iodine atom. In space group *Pnnm* this position would impose mirror symmetry on the molecule. However, in a subsequent difference-Fourier synthesis phased by this heavy atom, possible light-atom positions were too close to their mirror images. The space-group symmetry was relaxed to *Pnn*2 whereupon all the light-atom positions were located and successfully refined. Hydrogen atoms in the methyl groups were located in a difference Fourier, whilst the ring hydrogen atoms were placed in calculated positions (C–H 0.95 Å). In the final cycles of least-squares refinement, anisotropic temperature factors were used for all the non-hydrogen atoms with the hydrogen-atom parameters fixed. The weighting scheme used was $w = \{1 + [(F - 31)/19]^2\}^{-1}$. The refinement, including corrections for anomalous dispersion and extinction, converged to a final $R$ of 0.021 and weighted $R'$ of 0.026; in the final cycle, no parameter shift was greater than 20% of its standard deviation.

The final difference Fourier was featureless except for residual peaks up to 0.7 e Å$^{-3}$ near the iodine. The alternative ' hand ' of the molecule was rejected since it gave $R = 0.022$ and $R' = 0.026$, and distances around the iodine which should be equivalent were significantly different. The independent determination of (1) gave very similar molecular dimensions (at room temperature), but the co-ordinates are reported with the opposite hand $(1 - x,\ 1 - y,\ z$ relative to the present ones).[9]

(*b*) *Phenyliodine*(III) *bis*(*dichloroacetate*) (2).—A thin needle crystal was used for the data collection. Again, by cooling the crystal to −60 °C, the crystal decomposition was minimal.

*Crystal data.* $C_{10}H_7Cl_4IO_4$, Triclinic, $a = 10.462(3)$, $b = 4.870(2)$, $c = 15.445(5)$ Å, $\alpha = 101.03(3)$, $\beta = 99.89(3)$, $\gamma = 94.40(3)°$, $U = 756.0(5)$ Å$^3$, $D_m = 1.96$ g cm$^{-3}$ (flotation), $Z = 2$, $D_c = 2.02$ g cm$^{-3}$, Mo-$K_\alpha$ radiation $\lambda = 0.710\ 69$ Å, $\mu$(Mo-$K_\alpha$) = 28.49 cm$^{-1}$, $F(000) = 440$, −60 °C. Possible space groups are $P\bar{1}$ and $P1$.

Unit-cell dimensions and data were collected using a Syntex $P2_1$ diffractometer. Reflections were measured using θ—2θ scans over a scan range ($K_{\alpha_1}$ −1.2°) to ($K_{\alpha_2}$ +1.1°) to a maximum 2θ of 50° in two shells. The scan rate varied from 1.5 to 29.3° min$^{-1}$ and three standards were monitored every 100 reflections. The crystal was recentred after the first shell of data was completed. Towards the end of the data collection the crystal showed signs of decomposition and the data were rescaled in groups using equations (1)—(3). 2 685 Data were collected, of which 1 580 were considered observed [$I/\sigma(I) \geqslant 3.0$] and used in refinement.

$$F = F_0 \text{ for } t \leqslant 15.42 \text{ h} \qquad (1)$$

$$F = F_0{*}(1 + 0.004\ 498\ 5{*}t) \text{ for } 15.43 < t \leqslant 30.59 \text{ h} \qquad (2)$$

$$F = F_0{*}(1 - 0.000\ 53{*}t)[1 + (0.0181{*}t{*}\sin\theta)/\lambda] \text{ for } 30.59 \leqslant t \text{ h} \qquad (3)$$

Lorentz and polarisation corrections were applied. The absorption correction for the block-shaped crystal used is small and, because of the effects of crystal decomposition, no absorption correction was performed. The centrosymmetric space group $P\bar{1}$ was initially assumed and confirmed by a satisfactory refinement. From a difference-Fourier synthesis phased by an iodine atom located in a Patterson map, all the remaining heavy atoms were located. In the final cycles of least squares, anisotropic temperature factors were used for all the non-hydrogen atoms. Hydrogen atoms were included in calculated positions but were not refined. The weights used were $[1/\sigma(F)]^2$ for reflections within the ranges $10.0 \leqslant F \leqslant 21.5$ and $0.29 \leqslant \sin\theta \leqslant 0.65$. Reflections outside these ranges were given weights $w = X{*}Y{*}\,[1/\sigma(F)]^2$ where (*i*) $X = (\sin\theta)/0.29$ if $\sin\theta < 0.29$ or $X = 0.65/\sin\theta$ if $\sin\theta > 0.65$, and (*ii*) $Y = F/10.0$ if $F < 10.0$ or $Y = 21.5/F$ if $F > 21.5$. Four reflections with poor $w{*}(\Delta F)^2$ values after the application of this weighting scheme were rejected from subsequent refinement cycles. The refinement, including corrections for anomalous dispersion, converged to a final $R$ of 0.058 and $R'$ of 0.054.

The scattering factors for neutral I, Cl, O, C, and H used in the refinement of both compounds (1) and (2) were from ref. 12, in the analytical form. Computing was carried out with the ' *X*-Ray '72 ' system on a CDC 7600 computer and ' *X*-Ray '76 ' (1976) on a Burroughs B6700 computer.[13] Final positional parameters for all atoms in both (1) and (2) are listed in Table 1. The anisotropic temperature factors for these atoms with final structure factors for both compounds are available as Supplementary Publication No. SUP 22448 (23 pp.).† Bond lengths and angles are in Table 2, and information on molecular planes in Table 3.

## DISCUSSION

In both (1) and (2) the primary geometry of the trivalent iodine is the familiar T-shaped arrangement with covalent bonds to a phenyl ring and two oxygen atoms of the acetate groups. In (1) the I–O distances are the same (av. 2.156 Å) whilst in (2) they differ significantly

TABLE 1

Atomic co-ordinates (× 10$^4$) with standard deviations in parentheses

| Atom | *X* | *Y* | *Z* |
|---|---|---|---|
| (*a*) Compound (1) | | | |
| I | 9 508.5(2) | 7 393.9(3) | 0(0) |
| O(1) | 8 791(3) | 6 610(5) | 1 960(5) |
| O(2) | 10 023(4) | 7 127(7) | 3 069(6) |
| O(3) | 9 911(3) | 7 959(5) | −2 285(6) |
| O(4) | 11 106(3) | 8 549(5) | −1 072(6) |
| C(1) | 8 875(5) | 6 155(9) | 4 626(7) |
| C(2) | 9 294(4) | 6 664(8) | 3 160(8) |
| C(3) | 11 069(5) | 8 786(9) | −3 820(9) |
| C(4) | 10 705(4) | 8 424(6) | −2 268(8) |
| C(5) | 8 381(4) | 6 768(7) | −1 114(7) |
| C(6) | 7 846(4) | 7 971(7) | −1 643(8) |
| C(7) | 7 111(4) | 7 513(8) | −2 397(8) |
| C(8) | 6 933(4) | 5 955(10) | −2 641(8) |
| C(9) | 7 466(5) | 4 811(8) | −2 117(8) |
| C(10) | 8 205(4) | 5 210(7) | −1 318(8) |
| H(11) | 8 243 | 6 532 | 4 569 |
| H(12) | 9 188 | 6 660 | 5 452 |
| H(13) | 8 908 | 4 989 | 4 672 |
| H(31) | 10 981 | 9 757 | −3 937 |
| H(32) | 10 860 | 8 291 | −4 524 |
| H(33) | 11 524 | 8 985 | −3 802 |
| H(1) | 7 980 | 9 043 | −1 546 |
| H(2) | 6 733 | 8 313 | −2 815 |
| H(3) | 6 426 | 5 665 | −3 219 |
| H(4) | 7 335 | 3 736 | −2 347 |
| H(5) | 8 567 | 4 434 | −984 |
| (*b*) Compound (2) | | | |
| I | 4 256.8(8) | 119.0(16) | 1 405.9(5) |
| Cl(1) | 8 639(3) | 4 349(9) | 4 122(2) |
| Cl(2) | 6 143(4) | 5 816(12) | 4 407(2) |
| Cl(3) | 1 289(4) | −5 061(9) | −1 741(2) |
| Cl(4) | 1 093(4) | −8 047(8) | −325(2) |
| O(1) | 5 429(7) | 3 393(13) | 2 413(5) |
| O(2) | 6 831(10) | 394(21) | 2 708(7) |
| O(3) | 2 825(8) | −3 217(16) | 585(5) |
| O(4) | 3 869(12) | −2 677(31) | −495(6) |
| C(1) | 7 120(10) | 5 071(24) | 3 614(7) |
| C(2) | 6 441(12) | 2 669(25) | 2 880(7) |
| C(3) | 2 141(12) | −6 380(27) | −832(8) |
| C(4) | 3 042(13) | −3 886(30) | −212(8) |
| C(5) | 3 053(11) | −110(21) | 2 340(7) |
| C(6) | 3 413(13) | −1 547(27) | 3 006(9) |
| C(7) | 2 662(19) | −1 637(32) | 3 613(9) |
| C(8) | 1 578(19) | −495(38) | 3 547(10) |
| C(9) | 1 195(14) | 932(36) | 2 888(12) |
| C(10) | 1 942(14) | 1 129(28) | 2 260(9) |
| H(11) | 7 248 | 6 724 | 3 350 |
| H(31) | 2 710 | −7 749 | −1 049 |
| H(1) | 4 211 | −2 396 | 3 041 |
| H(2) | 2 884 | −2 556 | 4 107 |
| H(3) | 983 | −541 | 4 013 |
| H(4) | 335 | 1 704 | 2 823 |
| H(5) | 1 694 | 2 073 | 1 752 |

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

### Table 2

Bond lengths (Å) and bond angles (°) with standard deviations in parentheses *

(*a*) Bond lengths in (1)

(*i*) Around iodine

| | | | |
|---|---|---|---|
| I–O(1) | 2.159(5) | I · · · O(2) | 2.817(6) |
| I–O(3) | 2.153(5) | I · · · O(4) | 2.850(5) |
| I–C(5) | 2.090(6) | | |

(*ii*) Acetate groups

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1.506(10) | C(3)–C(4) | 1.507(10) |
| C(2)–O(1) | 1.316(8) | C(4)–O(3) | 1.307(8) |
| C(2)–O(2) | 1.211(9) | C(4)–O(4) | 1.227(8) |
| C(1)–H(11) | 1.04 | C(3)–H(31) | 0.84 |
| C(1)–H(12) | 0.97 | C(3)–H(32) | 0.82 |
| C(1)–H(13) | 0.99 | C(3)–H(33) | 0.73 |

(*iii*) Phenyl ring

| | | | |
|---|---|---|---|
| C(5)–C(6) | 1.400(8) | C(6)–H(1) | 0.94 |
| C(6)–C(7) | 1.384(9) | C(7)–H(2) | 0.97 |
| C(7)–C(8) | 1.368(11) | C(8)–H(3) | 0.97 |
| C(8)–C(9) | 1.361(10) | C(9)–H(4) | 0.96 |
| C(9)–C(10) | 1.396(10) | C(10)–H(5) | 0.92 |
| C(10)–C(5) | 1.361(8) | | |

(*b*) Bond angles in (1)

(*i*) Around iodine

| | | | |
|---|---|---|---|
| O(1)–I–O(3) | 164.0(2) | C(5)–I–O(2) | 131.9(2) |
| O(1)–I–C(5) | 81.4(2) | C(5)–I–O(4) | 132.7(2) |
| O(3)–I–C(5) | 82.6(3) | O(1)–I–O(4) | 145.8(2) |
| O(2)–I–O(4) | 95.2(2) | O(3)–I–O(2) | 145.2(2) |

(*ii*) Acetate groups

| | | | |
|---|---|---|---|
| I–O(1)–C(2) | 108.1(4) | I–O(3)–C(4) | 109.6(4) |
| O(1)–C(2)–O(2) | 121.7(6) | O(3)–C(4)–O(4) | 121.7(6) |
| O(1)–C(2)–C(1) | 114.1(6) | O(3)–C(4)–C(3) | 114.4(6) |
| O(2)–C(2)–C(1) | 124.2(7) | O(4)–C(4)–C(3) | 124.0(6) |
| I–O(2)–C(2) | 79.6(4) | I–O(4)–C(4) | 78.5(4) |

(*iii*) Phenyl ring

| | | | |
|---|---|---|---|
| I–C(5)–C(6) | 118.5(4) | C(7)–C(8)–C(9) | 120.6(6) |
| I–C(5)–C(10) | 118.7(4) | C(8)–C(9)–C(10) | 120.5(6) |
| C(5)–C(6)–C(7) | 116.9(6) | C(9)–C(10)–C(5) | 118.0(6) |
| C(6)–C(7)–C(8) | 121.1(6) | | |

(*c*) Bond lengths in (2)

(*i*) Around iodine

| | | | |
|---|---|---|---|
| I–O(1) | 2.136(6) | I · · · O(4) | 2.936(10) |
| I–O(3) | 2.163(7) | I–C(5) | 2.083(12) |
| I · · · O(2) | 3.049(10) | | |

(*ii*) Acetate groups

| | | | |
|---|---|---|---|
| Cl(1)–C(1) | 1.740(11) | Cl(3)–C(3) | 1.784(13) |
| Cl(2)–C(1) | 1.731(12) | Cl(4)–C(3) | 1.696(14) |
| C(1)–C(2) | 1.499(14) | C(3)–C(4) | 1.533(16) |
| C(2)–O(1) | 1.288(14) | C(4)–O(3) | 1.275(16) |
| C(2)–O(2) | 1.208(16) | C(4)–O(4) | 1.199(20) |
| C(1)–H(11) | 0.98 | C(3)–H(31) | 0.98 |

(*iii*) Phenyl ring

| | | | |
|---|---|---|---|
| C(5)–C(6) | 1.369(18) | C(6)–H(1) | 0.96 |
| C(6)–C(7) | 1.328(24) | C(7)–H(2) | 0.96 |
| C(7)–C(8) | 1.298(28) | C(8)–H(3) | 1.03 |
| C(8)–C(9) | 1.361(27) | C(9)–H(4) | 1.00 |
| C(9)–C(10) | 1.358(25) | C(10)–H(5) | 0.99 |
| C(10)–C(5) | 1.348(19) | | |

(*d*) Bond angles in (2)

(*i*) Around iodine

| | | | |
|---|---|---|---|
| O(1)–I–O(3) | 167.1(4) | C(5)–I–O(4′) | 130.0(4) |
| O(1)–I–C(5) | 86.0(3) | O(1)–I–O(4) | 143.3(3) |
| O(3)–I–C(5) | 82.5(3) | O(3)–I–O(4 ) | 116.8(3) |
| O(4)–I–O(4′) | 68.9(3) | I–O(4)–I′ | 111.1(4) |
| C(5)–I–O(4) | 157.8(4) | | |

### Table 2 (*Continued*)

(*d*) Bond angles in (2)

(*ii*) Acetate groups

| | | | |
|---|---|---|---|
| Cl(1)–C(1)–Cl(2) | 110.0(6) | Cl(3)–C(3)–Cl(4) | 111.4(7) |
| Cl(1)–C(1)–C(2) | 112.1(9) | Cl(3)–C(3)–C(4) | 106.7(10) |
| Cl(2)–C(1)–C(3) | 109.2(8) | Cl(4)–C(3)–C(4) | 114.7(9) |
| O(1)–C(2)–C(2) | 123.8(9) | O(3)–C(4)–O(4) | 124.5(11) |
| O(1)–C(2)–C(1) | 111.4(10) | O(3)–C(4)- C(3) | 115.8(12) |
| O(2)–C(2)–C(1) | 124.7(11) | O(4)–C(4)–C(3) | 119.7(12) |
| I–O(1)–C(2) | 116.2(6) | I–O(3)–C(4) | 111.5(8) |
| I–O(4)–C(4) | 75.8(7) | I–O(2)–C(2) | 73.3(7) |

(*iii*) Phenyl ring

| | | | |
|---|---|---|---|
| I–C(5)–C(6) | 118.7(9) | C(6)–C(7)–C(8) | 120.3(16) |
| I–C(5)–C(10) | 119.0(9) | C(7)–C(8)–C(9) | 122.1(18) |
| C(10)–C(5)–C(6) | 122.3(13) | C(8)–C(9)–C(10) | 119.8(16) |
| C(5)–C(6)–C(7) | 118.7(14) | C(9)–C(10)–C(5) | 116.7(14) |

* O(4′) is related to O(4) by $1 - x, -y, -z$.

### Table 3

Equations of the least-squares mean planes $PI + QJ + RK = S$ [a] in orthogonal angström space and deviations (Å) of atoms in square brackets. Atoms defining each plane are marked with an asterisk

(*a*) Compound (1)

Plane (1):

| P | Q | R | S |
|---|---|---|---|
| 0.4926 | 0.0197 | −0.8700 | −0.4418 |

[I * 0.018, C(5) * −0.015, C(6) * −0.005, C(7) * −0.006, C(8) * 0.017, C(9) * 0.010, C(10) * −0.021, O(1) −2.044, O(3) 2.081]

Plane (2):

| | | | |
|---|---|---|---|
| −0.2989 | 0.9387 | 0.1717 | −1.8387 |

[O(1) * 0.003, O(2) * 0.004, C(1) * 0.003, C(2) * −0.10, I −0.004, O(3) −0.087, O(4) 0.005, C(5) −0.141]

Plane (3):

| | | | |
|---|---|---|---|
| −0.3024 | 0.9493 | 0.0865 | −1.7736 |

[O(3) * 0.000, O(4) * 0.000, C(3) * 0.000, C(4) * −0.001, I −0.090, O(1) −0.232, O(2) −0.316, C(5) −0.143]

Plane (4):

| | | | |
|---|---|---|---|
| −0.3226 | 0.9350 | 0.1471 | −1.8555 |

[I * 0.039, O(1) * 0.033, O(2) * −0.038, O(3) * −0.012, O(4) * 0.008, C(1) −0.027, C(2) −0.025, C(3) −0.140, C(4) −0.043, C(5) * −0.030, C(6) 1.126, C(7) 1.038, C(8) −0.139, C(9) −1.248, C(10) −1.203]

Angles (°) between planes:

| | | | | | |
|---|---|---|---|---|---|
| (1)–(2) | 73.85 | (1)–(3) | 78.14 | (1)–(4) | 74.43 |
| (2)–(3) | 4.93 | (2)–(4) | 1.97 | (3)–(4) | 3.75 |

(*b*) Compound (2)

Plane (1):

| P | Q | R | S |
|---|---|---|---|
| 0.3372 | 0.8468 | 0.4114 | 2.2930 |

[I * 0.004, C(5) * 0.001, C(6) * −0.015, C(7) * 0.015, C(8) * −0.005, C(9) * 0.002, C(10) * −0.002]

Plane (2):

| | | | |
|---|---|---|---|
| −0.6477 | −0.3145 | 0.6940 | −1.3723 |

[O(1) * −0.007, O(2) * −0.009, C(1) * −0.006, C(2) * 0.023, I 0.191, C(5) 2.197]

Plane (3):

| | | | |
|---|---|---|---|
| 0.6542 | −0.6223 | 0.4298 | 3.3859 |

[O(3) * −0.002, O(4) * −0.003, C(3) * −0.002, C(4) * 0.007, I 0.160, O(1) 0.256, O(2) 2.447, C(5) −0.132]

Plane (4):

| | | | |
|---|---|---|---|
| 0.5352 | −0.6784 | 0.5033 | 3.2121 |

[I * 0.002, O(1) * −0.001, O(3) * −0.001, C(5) * 0.000, C(8) 0.079, C(2) 1.142, C(4) −0.711, O(2) 2.147, O(4) −0.302, O(4′) −0.523 [b]]

Angles (°) between planes:

| | | | | | |
|---|---|---|---|---|---|
| (1)–(2) | 78.51 | (1)–(3) | 82.55 | (1)–(4) | 79.22 |
| (2)–(3) | 85.97 | (2)–(4) | 77.53 | (3)–(4) | 8.64 |

[a] The orthogonal unit vector $I$ is parallel to $a$, $K$ is perpendicular to $a$ in the $ac$ plane, and $J$ is perpendicular to the $ac$ plane. [b] Related to O(4) by a centre of symmetry.

[2.136(6) and 2.163(7) Å]. The I–C distances in (1) and (2), however, are the same (2.08—2.09 Å). These bond lengths should be compared with values of 1.99 (I–O) and 2.10 Å (I–C) from the sum of the covalent radii. The corresponding C–I–O angles are 81.4(2) and 82.6(2)° for (1), 86.0(3) and 82.5(3)° for (2), so that the O–I–O angles are 164.0(2) and 167.1(4)°. This T-shaped arrangement of covalent bonds has been found in most compounds of $I^{III}$ investigated, and has been described by Gillespie and others as part of a trigonal-bipyramidal $AX_3E_2$ (E = lone pair) system with the phenyl group and two lone pairs equatorial.[14] However, in (1) and (2), as well as in the majority of the iodine(III) compounds studied, there are weak inter- and intra-molecular I · · · O contacts (secondary bonds), significantly less than the sum of the van der Waals radii for the atoms concerned, so that the $AX_3E_2$ trigonal-bipyramidal formulation of the geometry must be an incomplete description of the bonding.

In (1) and (2) the mode in which the I · · · O contacts are formed by each molecule is different. In (1) both I · · · O contacts [lengths 2.817(6) and 2.850(5) Å] are intramolecular, involving the second oxygen atoms of the acetate groups so that these groups may be classed as unsymmetrically bidentate or anisobidentate (Figure 1).* In (2), however, one acetate group is unidentate, and is rotated around the I–O bond, to make a dihedral angle of 78° with the C–I–$O_2$ plane, whilst the free oxygen atom of the other acetate group is involved in both inter- and intra-molecular contacts of the same length [2.936(10) Å] to two centrosymmetrically related iodine atoms. The molecules dimerise *via* a trapezoidal planar $I_2O_2$ ring with O–I–I′ and I–O–I′ angles of 68.9 and 111.1° respectively (Figure 2). In (1) the four acetate oxygen atoms and the I–C bond are coplanar and the plane of the phenyl ring makes a dihedral angle of 75° with this plane. In (2) the corresponding atoms around iodine deviate slightly more from a plane (maximum 0.5 Å) and the phenyl ring is at an angle of 79.2° (Table 3).

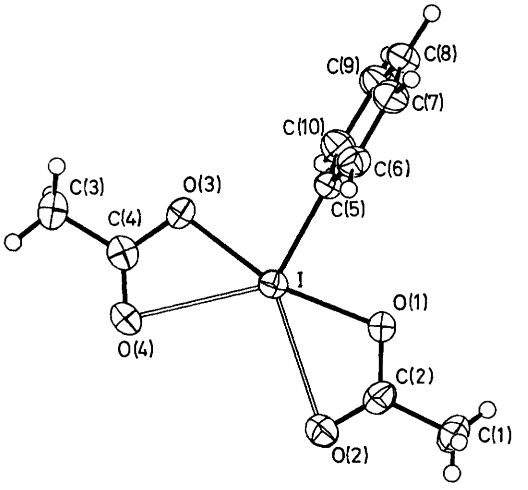

FIGURE 1 ORTEP view of molecule (1) down *b*, rotated 20° about *c*, showing the petangonal-planar arrangement of primary (filled) and secondary (unfilled) bonds

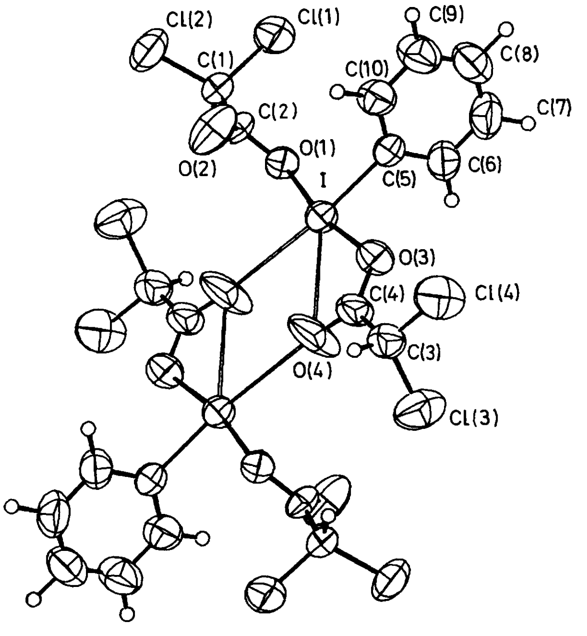

FIGURE 2 ORTEP view of molecule (2) down *b* showing bimolecular units linked by secondary bonds

Similar dimerisation *via* an $I_2O_2$ ring is found, in the α polymorph of 3-oxo-3*H*-1,2-benziodoxol-1-ium *m*-chlorobenzoate where the $I_2O_2$ ring has I–O distances of 2.82 Å (intra-) and 2.96 Å (inter-molecular), and in the α polymorph of 1-(2′-iodobenxoyloxy)-1,2-benziodoxol-3-(1*H*)-one where the two independent molecules in the asymmetric unit are related by a pseudo-centre, with I–O distances of 2.85 and 2.90 Å.[7] Both (1) and (2) (Figures 3 and 4) are packed in approximate columns stacked along *b*. In (1), pairs of molecules related by a two-fold axis have intermolecular I · · · O contacts (3.693 Å) virtually perpendicular to the main molecular plane, and these pairs of molecules form further intermolecular I · · · I′ $(-x, -1-y, z)$ contacts of 4.342 Å. In (2) the dimers stack in columns along *b* (separation 4.870 Å). This greater separation is due to the volume occupied by the unidentate acetate group.

The iodine co-ordination in (1) and (2) is the same as that in $(NO_3)PhIOIPh(NO_3)$.[1] There, for the T-shaped primary geometry, each iodine forms bonds to the phenyl ring, the bridging oxygen, and one oxygen of a nitrate group. The pentagonal-planar arrangement is then completed by two I · · · O contacts; one is intramolecular and the other involves the free oxygen atom of the nitrate group attached to the other iodine atom. However, the I–O(acid) and I · · · O distances (2.32 and 3.00 Å) are substantially longer than in (1) or (2). This must indicate that the degree of ionisation of the nitrate groups is greater than that of the acetate groups.

Apart from the pentagonal-planar arrangement of three primary and two secondary bonds described above,

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* The term anisobidentate was first used by J. L. K. F. de Vries and R. H. Herber (*Inorg. Chem.*, 1972, **11**, 2458) but is not common usage. For a classification of acetate co-ordination modes see N. W. Alcock, V. M. Tracey, and T. C. Waddington, *J.C.S. Dalton*, 1976, 2243.

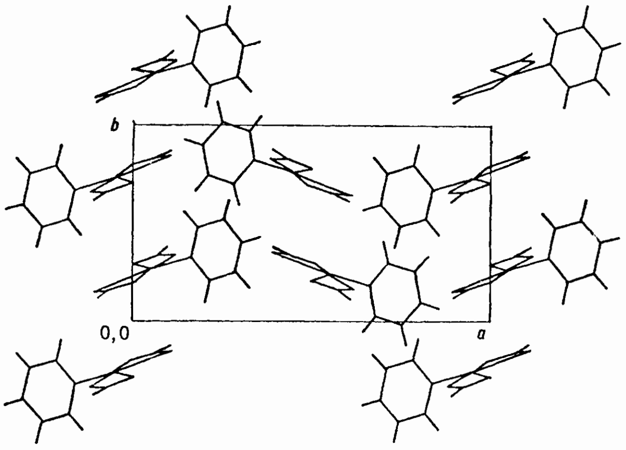

FIGURE 3 Packing diagram for (1), viewed down *c*

$I^{III}$ forms two types of square-planar arrangement. The first has three primary covalent bonds and one secondary bond as in $IPhCl_2$ and *N*-chloro-3*H*-1,2,3-benziodoxazol-1-ium chloride.[7] An alternative pattern of primary and secondary bonds has two short bonds and two longer ones. This is characteristic of the diphenyliodonium halides,[3] which are planar dimers, with the distances to the bridging halogen atoms intermediate between a single bond and a van der Waals contact; $I_2Cl_6$ is identical, apart from the replacement of the external phenyl groups by chlorine atoms.[15] The bonding arrangements found for iodine also occur with other non-metals as the central atom. The square-planar arrangement is quite common, either with three primary and one secondary bond, or two primary and two secondary bonds.[8] The former occurs, for example, in one crystalline form of bromo(ethylenethiourea)phenyltellurium(II) and bromo(ethyleneselenourea)phenyltellurium(II).[16] The arrangement of two primary and two secondary bonds is also found in several examples, particularly the complexes of the interhalogen cations $[ICl_2]^+$, $[BrF_2]^+$, and $[ClF_2]^+$ with the anions $[SbCl_6]^-$, $[AsF_6]^-$, and $[SbF_6]^-$.[8]

The pentagonal-planar geometry is much rarer for non-metal complexes, but with three primary and two secondary bonds the pentagonal plane is found for a few tellurium(II) and xenon(IV) compounds. The $[XeF_3]^+$ cation in $[XeF_3][SbF_6]$ is T-shaped with two axial Xe–F bonds (1.91 Å) and a shorter equatorial Xe–F bond (1.84 Å) and has been described as trigonal-bipyramidal $AX_3E_2$ (E = lone pair).[17] However, there are further Xe · · · F contacts of 2.49 and 2.71 Å to fluorine atoms in two neighbouring $[SbF_6]^-$ cations which are coplanar with the primary Xe–F bonds. In the case of $Te^{II}$, the anion $[Te(S_2COEt)_3]^-$ is pentagonal planar with *three* strong and *two* weaker bonds, involving two unsymmetrically bidentate and one unidentate ligands.[18] Other tellurium(II) compounds are known with *two* strong covalent bonds and *three* weaker intra- and intermolecular bonds coplanar with the covalent bonds. Thus in $Te(S_2CNEt_2)_2$ there is a planar $TeS_4$ group formed by the unsymmetrically bidentate ligands, and the fifth Te · · · S contact [3.579(5) Å] is made by a sulphur atom in a centrosymmetrically related molecule (with this atom 0.5 Å out of the plane defined by the $TeS_4$ group).[19] The crystal structures of $Te(S_2COMe)_2$ and $Te(S_2COEt)_2$ are similar:[20] planar $TeS_4$ groups with unsymmetrical Te–S distances and a fifth intermolecular contact (Te · · · S 3.51 and 3.61 Å respectively). The deviations of the S atoms forming these contacts from the planes defined by the $TeS_4$ groups are 1.10 and 0.65 Å respectively.

An equatorial arrangement of five pentagonal bonds of widely different strengths can also be found with an axial substituent so that the geometry is related to a pentagonal pyramid. In bis(1-oxopyridine-2-thiolato)phenylbismuth there is an intermolecular Bi · · · O of 3.37 Å completing the equatorial pentagonal plane of bonds.[21] In $[Pb(S_2COEt)_3]^-$ an equatorial plane of two strong and three weak Pb–S distances occurs with a further axial bond.[22] There is even one example with two axial groups, $TlMe_2(S_2COMe)_2$, which has three intermolecular contacts in the same plane as the primary Tl–S bonds.[23]

*Bonding Models.*—Three possible bonding models can be considered for these pentagonal-planar systems containing bonds of very different lengths. The simplest treats the primary covalent bonds as two-centre two-electron bonds, and any additional interactions are considered to be electrostatic. This model, however, fails to explain why the primary and secondary bonds in

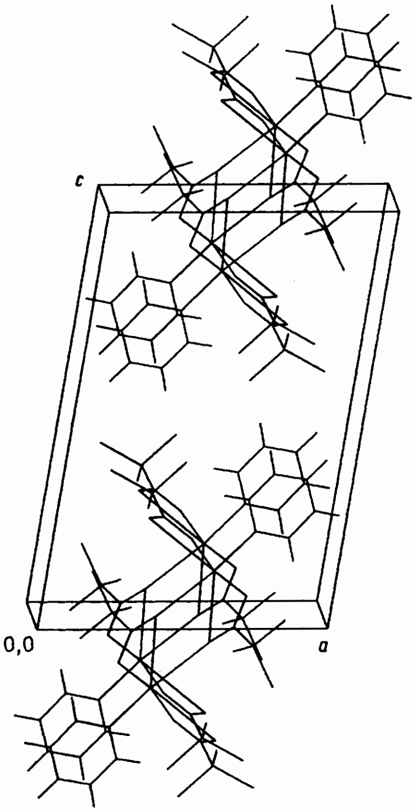

FIGURE 4 Packing diagram for (2), viewed perpendicular to the *ac* plane

these systems are essentially coplanar;[19] it would be expected that many other positions around the central atom would be of approximately equal energy.

Secondly, it has been proposed that the anion $[Te(S_2COEt)_3]^-$ might represent an $AX_5E_2$ system on the Gillespie–Nyholm model.[18] With two lone pairs, the expected geometry would presumably be the pentagonal-planar arrangement. The two lone pairs would be in axial positions perpendicular to the plane, minimising lone-pair–bond-pair interactions, since the alternative of equatorial lone pairs would give (with all bonds equal) lone-pair–bond-pair angles of 72° in the plane. The drawback of this model is the difference in strength between the strong and weak bonds, where equal bonds would be expected. One explanation for this, advanced to explain the asymmetric ligands in $[Te(S_2COEt)_3]^-$ and related complexes, is that the repulsion between the bonding electrons of the shortest Te–S bond (to the unidentate ligand) and the axial lone pairs is stronger than other lone-pair–bond-pair interactions; this forces the lone pairs into an off-axial position, away from the unidentate ligand. The two Te–S bonds furthest from the unidentate ligand then lengthen as a consequence of the increased repulsion from these off-axial lone pairs. The asymmetry in the short Te–S bond lengths (one of 2.50 Å and two of 2.66 Å) seems, however, much too modest to account for the substantial lengthening of the two other Te $\cdots$ S bonds (3.055 Å).

An alternative explanation for the difference in the bond lengths might be overcrowding, leading to partial expulsion of one or two ligands. A useful comparison here is with uranyl complexes, which often have pentagonal-planar co-ordination around the axial $[UO_2]^{2+}$ group. The geometrical constraints of these complexes are fairly well understood and it appears that non-bonded O $\cdots$ O contacts of 2.6—2.8 Å are the minimum required for avoiding distortions due to overcrowding which, if sufficiently strong, will cause expulsion of a ligand.[24] In (1) the non-bonded O $\cdots$ O contact in the $AX_5$ plane is 4.2 Å, whilst in (2) it is 3.32 Å. These will clearly not impose any steric contraints.

By a third approach, I $\cdots$ O and Te $\cdots$ S interactions can be described using the secondary-bonding model. In its normal form a linear X–A $\cdots$ Y system is explained by the overlap of the $\sigma^*$ orbital of the primary bond with a lone-pair orbital (*e.g.* the *p* orbital of Cl in $IPhCl_2$). However, in the pentagonal-planar examples, the long inter- and intra-molecular contacts are far from being collinear with a covalent bond; typical O–I $\cdots$ O, Cl–I $\cdots$ O, or S–Te $\cdots$ S angles are in the range 140—150°.

It is, however, possible to modify the secondary-bonding model to account for this geometry by considering the overlap of the I–C $\sigma^*$ orbital not with *one* lone-pair orbital but with *two*. Thus, two 'unco-ordinated' oxygen atoms give *two* filled weakly bonding orbitals concentrated between the heavy atom and the oxygen atoms (Figure 5). The resulting molecular orbitals resemble the three-centre bonding orbitals used to describe the triangular faces in boranes.[25] This model accounts for the bonding in all the species such as $[XeF_3][SbF_6]$, with three strong and two weaker bonds. For the tellurium(II) compounds with two strong and three weak bonds, the secondary-bonding description requires the formation of three-centre systems involving three lone pairs on sulphur atoms overlapping with two $\sigma^*$ orbitals of the strong covalent Te–S bonds (Figure 5). (In contrast to the $AX_3E_2$ species already mentioned, the primary geometry here falls into the $AX_2E_2$ class, with the lone pairs above and below the pentagonal plane.)

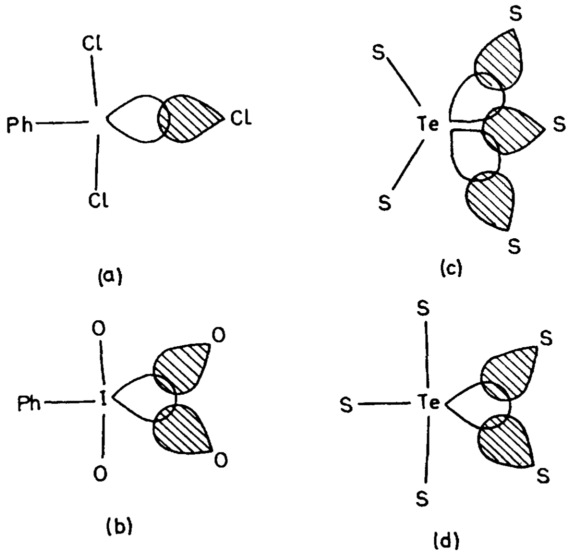

FIGURE 5 Alternative arrangements with two- or three-centre overlap to form secondary bonds. Hatched orbitals are filled, the others are empty. (*a*) Standard linear secondary bond, (*b*) pentagonal plane around I, (*c*) pentagonal plane around Te with two short bonds, and (*d*) pentagonal plane around Te with three short bonds

This three-centre overlap model can be used to rationalise other examples of anomalously long interactions. For example, the crystal structure of the pharmaceutically important molecule trichlorotris(6-methoxy-3-sulphanilamidopyridazine)trichlorotris(6-methoxy-3-sulphanilamidopyridazine)bismuth(III) has three-fold symmetry, lying on the axis in space group *R*3, and contains $BiCl_3$ groups loosely bound to the organic molecule by Bi $\cdots$ N and Bi $\cdots$ O contacts much longer than the sum of covalent or ionic radii [Bi–N 2.90(1), Bi–O 3.09(2) Å].[26] The geometry about bismuth can be described as a distorted octahedron of three chlorine and three nitrogen atoms. However, there are also the three oxygen atoms at roughly the same distance as the nitrogen atoms. The Cl–Bi–O and Cl–Bi–N angles are 139.8(3) and 162.6(3)°, and could indicate three-centre overlap between the nitrogen and oxygen lone pairs with the Bi–Cl $\sigma^*$ orbital; the resulting bond [2.53(1) Å] is slightly longer than the sum of the covalent radii (2.45 Å). The interactions occurring in $BiCl_3$ itself[27] can perhaps also be described by three-centre overlaps.

In differentiating between the alternative explanations of the geometries of (1) and (2) in terms of an $AX_5E_2$

system with axial lone pairs, or an $AX_3E_2$ system with two secondary bonds (forced into the same plane as the primary bonds by repulsion from the pseudo-axial lone pairs), the balance appears to lie towards the latter. In particular, it appears to offer a more satisfactory explanation for the essentially undisturbed T-shaped geometry of the primary bonds, and the large difference in bond length between the primary and secondary bonds.

Irrespective of the detailed model preferred, one important empirical correlation is clear: the effect of changing from halogenoiodine(III) to oxoiodine(III) compounds. In all examples of $IRX_2$ compounds so far studied, this produces a conversion from square-planar into pentagonal-planar co-ordination. Following the secondary-bonding model, this might be attributed to the greater accessibility of the lone pair on oxygen. However, the comparison of (1) and (2) also shows that the secondary bonds are very sensitive to slight changes in ligands, and the resulting conformational effects can be considerable. Similar conclusions have been reached on the basis of i.r. and Mössbauer spectral evidence, particularly for organotellurium compounds.[27]

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