# Secondary Bonding. Part 4.[1] The Crystal and Molecular Structure of μ-Oxo-bis[nitrato(phenyl)iodine(III)]

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The crystal and molecular structure of the title compound has been determined from diffractometer data by the heavy-atom method. The crystals (α-form) are monoclinic, space group *Cc*, with unit-cell dimensions $a$ = 16.145(9), $b$ = 7.067(7), $c$ = 15.058(18) Å, β = 108.72(8)°, $Z$ = 4, from 1 337 observed reflections, $R$ = 0.063. The oxygen-bridged molecular structure is confirmed with average dimensions I–O(bridge) 2.00(5), I–O($NO_3$) 2.32(3) Å, I–O–I 123.7(6)°, and I–C 2.05(2) Å. The primary geometry around each iodine is T-shaped, but two secondary I · · · O bonds [3.01(2) Å] convert this into a pentagonal plane.

THE reaction of nitric acid and a phenyliodine(III) compound was originally reported [2] to give the simple dinitrate $IPh(NO_3)_2$. However, accurate analysis and spectroscopic study [3] later showed this to be a μ-oxo-species $(NO_3)PhIOIPh(NO_3)$. Such species have been shown to be characteristic of the iodine(III) complexes with strong acids,[3] although only the nitrate is readily isolable. We have now determined the crystal structure of compound (1), μ-oxo-bis[nitrato(phenyl)iodine(III)], the first μ-oxo-iodine species to be reported. The crystals also contain I · · · O secondary bonds of an unusual type.

## EXPERIMENTAL

Compound (1) was prepared by the method of Dasent and Waddington.[3] It can be recrystallized from benzene. It exists in two modifications, monoclinic (α) and triclinic (β); the former was produced more frequently, but it was not possible to establish their relative stability or reproducible conditions for their formation. Both forms have plate-like crystals.

*Crystal Data.*—$C_{12}H_{10}I_2N_2O_7$, α form, Monoclinic, space group *Cc*, $a$ = 16.143(9), $b$ = 7.067(7), $c$ = 15.058(18) Å, β = 108.72(8)°, $U$ = 1 627(3) Å$^3$, $Z$ = 4, $D_c$ = 2.24 g cm$^{-3}$, $F(000)$ = 258, Mo-$K_\alpha$ radiation with a graphite monochromator, λ = 0.710 69 Å, μ = 39.6 cm$^{-1}$.

β form, Triclinic, space group $P\bar{1}$, $a$ = 16.43(2), $b$ = 12.440(2), $c$ = 8.483(1) Å, α = 91.13(1), β = 101.31(1), γ = 93.16(1)°, $U$ = 1 696.9(4) Å$^3$, $Z$ = 4, $D_c$ = 2.14 g cm$^{-3}$.

Unit-cell constants were determined by least-squares fit to the positions of 15 reflections, using the standard programs of a Syntex $P2_1$ four-circle diffractometer. For the α form, data were collected with this instrument to $2\theta$ = 50°, with variable scan rates of 2—29° min$^{-1}$ depending on the intensity for a 2-s prescan; the total background time was half the scan time. A scan width ($2\theta$) of $2.4 + (\alpha_2 - \alpha_1)$ was used. A few strong reflections were remeasured at low current to avoid coincidence losses. The temperature was held at −56 °C with the Syntex LT-1 device to prevent decomposition by *X*-rays. The intensity of three standards measured every 100 reflections showed no significant change.

Lorentz, polarization, and absorption corrections were applied (the last with the program ABSCOR [4]), and refinement was carried out on the 1 337 reflections having $I/\sigma(I) > 3.0$. Systematic absences $hkl$ with $h + k = 2n$ and $h0l$ with $l = 2n$ indicate space groups $C2/c$ or $Cc$, and the structure was successfully refined in the latter. Positions for two iodine atoms were found from the Patterson function, and the remaining atoms found from difference-Fourier synthesis using the program SHELX-76. In the final cycles of refinement using the '*X*-RAY '76' programs,[5] the phenyl groups were treated as rigid bodies and the iodine and bridging oxygen were refined anisotropically. An empirical weighting scheme was used, giving reduced weight to reflections with high and low $F$ and sin θ. Refinement in the first chosen configuration converged with $\Sigma[w(F_o - F_c)]^2 = 0.4239 \times 10^5$. The structure was then changed to the opposite hand and this refined to $R = 0.063$, $\Sigma[w(F_o - F_c)]^2 = 0.4166 \times 10^5$. The second configuration was therefore taken as the correct one. Scattering factors were taken from ref. 6, in the analytical form.

Table 1 contains the atomic co-ordinates, Table 2 the bond lengths and angles, and Table 3 the molecular planes. Temperature factors and structure factors are listed in Supplementary Publication No. SUP 22447 (10 pp.).†

For the β form, the unit cell was determined and data collection started, but the crystal was lost due to malfunction of the low-temperature device, and satisfactory crystals could not be found to continue the determination. However, from partial photographic data (layers of $l$ = 0, 1, and 2), the co-ordinates of four independent iodine atoms were found (by hand-applied direct methods) as: 0.133, 0.068, 0.150; 0.120, 0.293, −0.082; 0.656, 0.025, 0.190; and 0.363, 0.098, 0.544. Refinement starting from these showed

TABLE 1

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

| | $X$ | $Y$ | $Z$ |
|---|---|---|---|
| I(1) | 0 | −202(4) | −2 500 |
| I(2) | −1 773.6(9) | −209.3(37) | −1 603.3(12) |
| O(100) | −823(26) | 1 127(16) | −2 002(38) |
| N(1) | 1 681(31) | −1 791(62) | −2 738(31) |
| N(2) | −3 429(21) | −1 740(42) | −1 232(22) |
| O(11) | 1 926(15) | −1 080(32) | −2 039(17) |
| O(12) | 846(16) | −1 632(31) | −3 309(17) |
| O(13) | 2 158(19) | −2 614(38) | −3 115(20) |
| O(21) | −3 688(15) | −500(32) | −1 859(16) |
| O(22) | −2 557(15) | −1 949(32) | −844(17) |
| O(23) | −3 846(18) | −2 907(35) | −894(19) |
| C(11) | −929(13) | −1 974(24) | −3 353(14) |
| C(12) | −1 646(15) | −1 318(23) | −4 089(17) |
| C(13) | −2 308(14) | −2 575(34) | −4 572(16) |
| C(14) | −2 252(14) | −4 488(31) | −4 320(17) |
| C(15) | −1 533(16) | −5 153(21) | −3 683(18) |
| C(16) | −874(14) | −3 887(27) | −3 101(15) |
| C(21) | −854(14) | −1 969(25) | −746(17) |
| C(22) | −914(13) | −3 941(26) | −836(15) |
| C(23) | −248(15) | −5 085(20) | −262(16) |
| C(24) | 477(14) | −4 257(27) | 401(14) |
| C(25) | 536(13) | −2 286(28) | 491(14) |
| C(26) | −129(15) | −1 142(20) | −83(17) |

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

TABLE 2

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

| | | | |
|---|---|---|---|
| I(1)–O(100) | 1.96(5) | I(1)–O(100)–I(2) | 123.7(6) |
| I(2)–O(100) | 2.05(5) | O(100)–I(1)–O(12) | 171(1) |
| I(1)–O(12) | 2.33(3) | O(12)–I(1)–C(11) | 80.9(8) |
| I(1)–C(11) | 2.06(2) | O(100)–I(1)–C(11) | 94(1) |
| I(2)–O(22) | 2.31(3) | O(100)–I(2)–O(22) | 166(1) |
| I(2)–C(21) | 2.05(2) | O(100)–I(2)–C(21) | 90(1) |
| N(1)–O(11) | 1.12(5) | O(22)–I(2)–C(21) | 76.5(9) |
| N(1)–O(12) | 1.35(5) | O(12)–N(1)–O(13) | 113(4) |
| N(1)–O(13) | 1.24(6) | O(12)–N(1)–O(11) | 123(5) |
| N(2)–O(21) | 1.26(4) | O(13)–N(1)–O(11) | 124(4) |
| N(2)–O(22) | 1.35(4) | | |
| N(2)–O(23) | 1.27(5) | O(21)–N(2)–O(22) | 117(3) |
| C–C | 1.40 (fixed) | O(21)–N(2)–O(23) | 131(3) |
| | | O(22)–N(2)–O(23) | 112(3) |
| | | C–C–C | 120 (fixed) |
| Secondary bonds | | | |
| I(1) · · · O(11) | 3.02(2) | O(11) · · · I(1)–O(12) | 45.6(6) |
| I(1) · · · O(23′) | 3.01(2) | O(11) · · · I(1) · · · O(23′) | 66.4(7) |
| I(2) · · · O(21) | 3.00(2) | O(23′) · · · I(1)–O(100) | 75.8(12) |
| I(2) · · · O(13′) | 3.00(3) | O(21) · · · I(2)–O(22) | 47.3(7) |
| | | O(21) · · · I(2) · · · O(13′) | 68.1(8) |
| | | O(13′) · · · I(2)–O(100) | 78.3(11) |

approximate positions for the remaining atoms with similar geometry to the α form, but could not be carried to completion. In particular, the presence of solvent in the crystal cannot be exluded.

## RESULTS AND DISCUSSION

The primary structure confirms the suggested $I^{III}$–O–$I^{III}$ unit. The shortest bonds to the iodine atoms have a T-shaped arrangement, but there are two longer I · · · O secondary bonds completing pentagonal planes. For each iodine one of these secondary bonds is intramolecular, a link to the second oxygen atom of the nitrate group, and as a result the O–I · · · O angles are rather small (46 and 47°). The other bond is intermolecular, to the third oxygen atom of the adjacent nitrate group, holding the molecules together in chains (Figure 2). The significance of the I · · · O bonds is considered in the following paper, in conjunction with other examples.

The nitrate groups make angles of only a few degrees to the ($IO_4C$) planes (Table 3). Thus there could be some π interaction, but this arrangement seems more likely to be due to steric requirements. In contrast, the ends of the molecule are twisted around O(100) so that the two ($IO_4C$) planes have a dihedral angle of almost 90°.

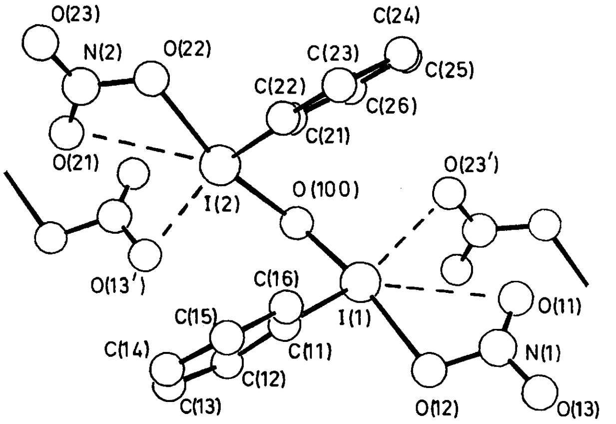

FIGURE 1 View of the molecule with the atomic numbering. The I · · · O secondary interactions are shown as broken lines

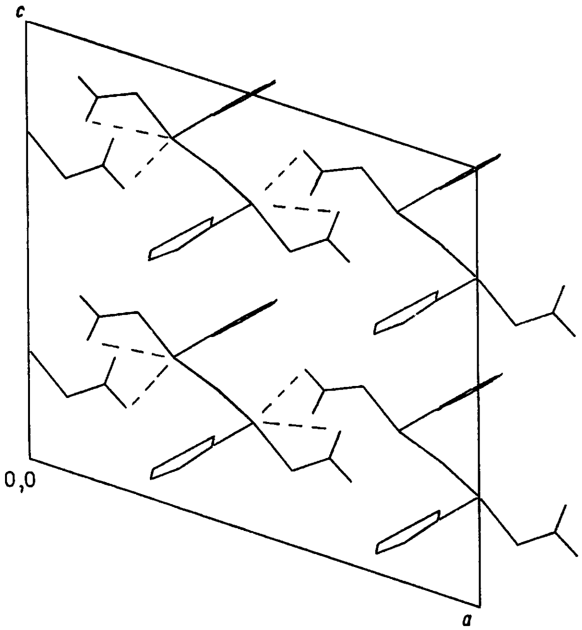

FIGURE 2 Packing diagram, viewed down *b*

The I–C distance (2.05 Å) is similar to values found in the diphenyliodonium halides[7] (2.08—2.10 Å) and, allowing for the difference in covalent radii,* the I–O-(bridge) distance (2.00 Å) has the value that would be predicted from the I–C distance; the difference between the individual values is not significant. However, the I–O–I angle (123.7°) suggests that there may be some π interaction between the *p* orbitals of this O and the *d*

TABLE 3

Least-squares planes (in orthogonal Ångstrom space; *X* is parallel to *a*, *Y* is perpendicular to *a* in the *ac* plane, and *Z* is orthogonal) and deviations (Å) from the planes in square brackets

Plane (1):
$-0.176X - 0.749Y + 0.639Z = -2.298$
[I(1) −0.09, O(12) −0.38, O(100) −0.06, O(23′) −0.03, O(11) 0.29, C(11) 0.26]

Plane (2):
$-0.118X + 0.709Y + 0.696Z = -1.474$
[I(2) 0.02, O(22) 0.10, O(100) 0.09, O(13′) −0.06, O(21) −0.03, C(21) −0.13]

Plane (3):
$-0.346X - 0.850Y + 0.397Z = -1.909$
[N(1) 0.04, O(12) −0.01, O(11) −0.01, O(13) −0.01]

Plane (4):
$-0.245X + 0.670Y + 0.700Z = -0.852$
[N(2) 0.01, O(22) 0.00, O(21) 0.00, O(23) 0.00]

Dihedral angles (°):

| | | | |
|---|---|---|---|
| (1)–(3) | 18.0 | (2)–(4) | 7.6 |
| (1)–(2) | 86.3 | | |

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* Obtained by comparing for example, C–C and C–O; L. E. Sutton, 'Table of Interatomic Distances,' *Special Publ.*, The Chemical Society, London, 1965, no. 18.

orbitals on I. The I–O($NO_3$) distances (2.32 Å) show that the bonding to the nitrate must be weak, and presumably partly ionic. The errors in the N–O distances are too large to show any distinction between the three N–O bonds.

There is only one other oxygen-bridged iodine(III) compound whose structure has been reported,[8] $(IO)_2SO_4$. This has I–O(bridge) 1.97 (av.), I–O($SO_4$) 2.39 Å (av.), and O–I–O 95.2°. Thus, the pattern repeated is of a short bridged distance and a longer one to the anion, but the bridge angle is considerably smaller. Larger angles are found [9] in the bridged iodine(V) species, $I_2O_5$ and its adduct $HIO_3{\cdot}I_2O_5$ (139.2 and 125.6°), but despite the change in oxidation state the I–O(bridge) distances are not much smaller (av. 1.93 and 1.96 Å). Further structural results will be needed before the significance of these parameters becomes clear.

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