Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

| | | | | | |
|---|---|---|---|---|---|
| O(1)—C(2) | 1·376 (3) | O(1)—C(11) | 1·425 (4) | O(2)—C(1) | 1·392 (2) |
| O(2)—C(12) | 1·352 (3) | O(3)—C(12) | 1·186 (3) | O(4)—C(14) | 1·445 (3) |
| O(4)—C(15) | 1·344 (4) | O(5)—C(15) | 1·197 (4) | O(6)—C(17) | 1·229 (4) |
| O(7)—C(19) | 1·457 (5) | O(7)—C(20) | 1·345 (5) | O(8)—C(20) | 1·182 (6) |
| N(1)—C(7) | 1·464 (3) | N(1)—C(8) | 1·479 (3) | N(1)—C(17) | 1·366 (3) |
| C(1)—C(2) | 1·390 (3) | C(1)—C(6) | 1·386 (3) | C(2)—C(3) | 1·397 (4) |
| C(3)—C(4) | 1·380 (4) | C(3)—C(10) | 1·508 (4) | C(4)—C(5) | 1·380 (4) |
| C(5)—C(6) | 1·399 (3) | C(5)—C(9) | 1·507 (4) | C(6)—C(7) | 1·504 (3) |
| C(7)—C(14) | 1·527 (3) | C(8)—C(9) | 1·537 (4) | C(8)—C(19) | 1·519 (5) |
| C(12)—C(13) | 1·494 (4) | C(15)—C(16) | 1·473 (4) | C(17)—C(18) | 1·496 (4) |
| C(20)—C(21) | 1·469 (8) | | | | |

| | | | |
|---|---|---|---|
| C(2)—O(1)—C(11) | 114·5 (2) | C(1)—O(2)—C(12) | 118·1 (2) |
| C(14)—O(4)—C(15) | 116·4 (2) | C(19)—O(7)—C(20) | 120·0 (3) |
| C(7)—N(1)—C(8) | 119·7 (2) | C(7)—N(1)—C(17) | 122·1 (2) |
| C(8)—N(1)—C(17) | 117·1 (2) | O(2)—C(1)—C(2) | 119·7 (2) |
| O(2)—C(1)—C(6) | 118·4 (2) | C(2)—C(1)—C(2) | 121·6 (2) |
| O(1)—C(2)—C(1) | 119·5 (2) | O(1)—C(2)—C(3) | 120·2 (2) |
| C(1)—C(2)—C(3) | 120·2 (2) | C(2)—C(3)—C(4) | 117·4 (2) |
| C(2)—C(3)—C(10) | 121·1 (3) | C(4)—C(3)—C(10) | 121·5 (3) |
| C(3)—C(4)—C(5) | 123·2 (2) | C(4)—C(5)—C(6) | 119·3 (2) |
| C(4)—C(5)—C(9) | 124·1 (2) | C(6)—C(5)—C(9) | 116·6 (2) |
| C(1)—C(6)—C(5) | 118·3 (2) | C(1)—C(6)—C(7) | 122·5 (2) |
| C(5)—C(6)—C(7) | 119·2 (2) | N(1)—C(7)—C(6) | 110·2 (2) |
| N(1)—C(7)—C(14) | 114·1 (2) | C(6)—C(7)—C(14) | 109·5 (2) |
| N(1)—C(8)—C(9) | 112·6 (2) | N(1)—C(8)—C(19) | 111·8 (2) |
| C(9)—C(8)—C(19) | 111·0 (2) | C(5)—C(9)—C(8) | 113·9 (2) |
| O(2)—C(12)—O(3) | 122·6 (2) | O(2)—C(12)—C(13) | 111·0 (2) |
| O(3)—C(12)—C(13) | 126·3 (2) | O(4)—C(14)—C(7) | 111·8 (2) |
| O(4)—C(15)—O(5) | 123·0 (3) | O(4)—C(15)—C(16) | 112·8 (3) |
| O(5)—C(15)—C(16) | 124·2 (3) | O(6)—C(17)—N(1) | 119·6 (2) |
| O(6)—C(17)—C(18) | 120·5 (3) | N(1)—C(17)—C(18) | 119·9 (2) |
| O(7)—C(19)—C(8) | 106·9 (3) | O(7)—C(20)—O(8) | 121·9 (5) |
| O(7)—C(20)—C(21) | 112·7 (4) | O(8)—C(20)—C(21) | 125·3 (4) |

| | | | |
|---|---|---|---|
| C(8)—N(1)—C(7)—C(6) | −45·6 (3) | C(17)—N(1)—C(7)—C(14) | −114·3 (2) |
| C(7)—N(1)—C(8)—C(9) | 8·7 (3) | C(17)—N(1)—C(8)—C(19) | 74·7 (3) |
| C(9)—C(5)—C(6)—C(7) | 2·8 (3) | C(6)—C(5)—C(9)—C(8) | −41·6 (4) |
| C(5)—C(6)—C(7)—N(1) | 39·9 (3) | N(1)—C(8)—C(9)—C(5) | 35·1 (3) |
| C(19)—C(8)—C(9)—C(5) | 161·3 (3) | | |

length 1·389 Å and r.m.s. deviation 0·004 Å. The N(1)—C(7) bond which is *trans* to the O(6) carbonyl group is significantly shorter than N(1)—C(8). Asymmetry of the exocyclic bond angles around the N(1) and C(7) atoms is observed. The adjacent angles C(7)—N(1)—C(17) and N(1)—C(7)—C(14) are significantly larger than C(8)—N(1)—C(17) and C(6)—C(7)—C(14), respectively. The exocyclic bond angles around C(8), however, are almost symmetrical. In the packing there are no intermolecular contacts less than the sum of the van der Waals radii.

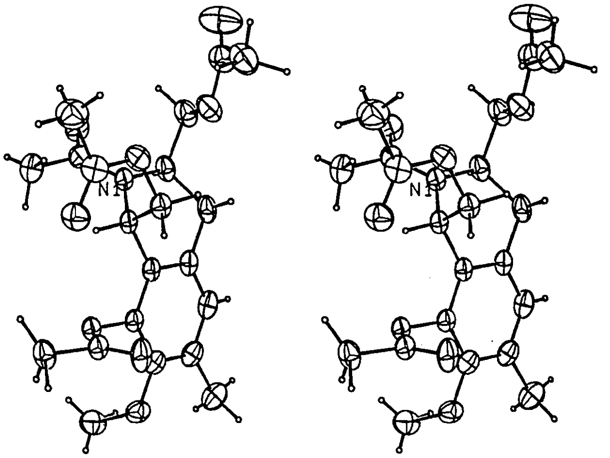

Fig. 1. Stereoview of the molecule with thermal ellipsoids at 30% probability.

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# Structure of *N*-Iodosuccinimide

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**Abstract.** $C_4H_4INO_2$, $M_r = 224{\cdot}99$, tetragonal, $P4_1$ or $P4_3$, $a = 6{\cdot}339\,(1)$, $c = 15{\cdot}455\,(4)$ Å, $V = 621{\cdot}0\,(2)$ Å$^3$, $Z = 4$, $D_x = 2{\cdot}406$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 50{\cdot}11$ cm$^{-1}$, $F(000) = 416$, $T = 295$ K, $R = 0{\cdot}019$ for 617 observed reflections [$I > 2{\cdot}58\sigma(I)$] and 77 parameters for the structure refined in $P4_1$. The

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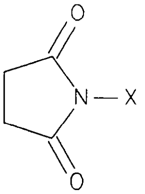
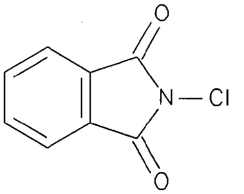
crystal structure is stabilized by strong intermolecular I···O interactions. The calculated polarization of a single crystal together with the results of a Kundt–Bürker pyroelectric test lead to an assignment of the absolute orientation of the molecules along the polar axis.

**Introduction.** *N*-Iodosuccinimide (I-1) had been reported to belong to the ditetragonal pyramidal class (point group 4*mm*) of crystals (Groth, 1910). No detailed X-ray investigation had been carried out on this simple compound even though the X-ray structures of the parent compound [succinimide (H-1), orthorhombic, *Pbca*] (Mason, 1961) and other *N*-halogen substituted compounds, *N*-chloro-[(Cl-1), $P2_12_12_1$] (Brown, 1961) and *N*-bromosuccinimide [(Br-1), $P2_12_12_1$] (Jabay, Pritzkow & Jander, 1977), have been determined. We were interested in the structure of this compound in connection with studies correlating absolute atomic arrangement with crystal morphology and the sense of electric polarization (Curtin & Paul, 1982, 1987; Pennington, Chakraborty, Paul & Curtin, 1988). The presence of a polar axis had been deduced from crystal morphology and by the presence of a strong pyroelectric effect (Groth, 1910).



(H-1) $X = \mathrm{H}$
(Cl-1) $X = \mathrm{Cl}$
(Br-1) $X = \mathrm{Br}$
(I-1) $X = \mathrm{I}$



(2)

**Experimental.** *N*-Iodosuccinimide was purchased from Aldrich. Although the crystals were relatively stable in a suitably colored glass bottle they quickly showed signs of decomposition when exposed to ambient light. Colorless crystals were obtained from acetone.* Crystal 0·45 × 0·26 × 0·26 mm; Syntex $P2_1$ diffractometer; graphite-monochromatized Mo *Kα* radiation; cell parameters refined from diffractometer angles for 15 centered reflections ($25 < 2\theta < 27°$). Intensity data collected by $\omega/2\theta$ scans for 1671 reflections with $3 < 2\theta < 53°$ (*h*, −7 to 7; *k*, 0 to 7; *l*, 0 to 19); three standard reflections monitored (± 2%). Lorentz–polarization corrections and an analytical absorption correction (de Meulenaer & Tompa, 1965), min. and max. transmission factors 0·31–0·39, 666 unique reflections ($R_{\rm int} = 0{\cdot}038$), 617 counted as observed [$I > 2{\cdot}58\sigma(I)$]. Structure solved by the Patterson method in *SHELXS*86 (Sheldrick, 1986). I atom located from the Patterson map, the other non-H atoms by subsequent difference Fourier synthesis. Space group initially considered as $P4_1$. H atoms fixed in their idealized positions with individual isotropic thermal parameters. Full-matrix least-squares refinement, positional and anisotropic thermal parameters for all non-H atoms, isotropic thermal parameters for H atoms. Final $R = 0{\cdot}019$, 77 parameters, 617 observations, $wR = 0{\cdot}026$, $w = \{3{\cdot}56/[\sigma^2(F_o) + 0{\cdot}0004F_o^2]\}$, $S = 1{\cdot}168$, $(\Delta/\sigma)_{\max} = 0{\cdot}001$, $\Delta\rho$ within 0·41 and $-0{\cdot}45$ e Å$^{-3}$. Positional parameters are presented in Table 1.*

Table 1. *Final positional parameters and equivalent isotropic thermal parameters for non-*H *atoms and isotropic thermal parameters for* H *atoms, of N-iodosuccinimide*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | *x* | *y* | *z* | $U_{\rm eq}$(Å$^2$) |
|---|---|---|---|---|
| I | 0·20615 (6) | −0·12620 (5) | 0·5000† | 0·0411 |
| O(1) | 0·6044 (10) | −0·1017 (9) | 0·3676 (4) | 0·0584 |
| O(2) | 0·0374 (10) | 0·3162 (9) | 0·4165 (5) | 0·0766 |
| N | 0·3125 (8) | 0·0813 (8) | 0·4072 (4) | 0·0377 |
| C(1) | 0·4931 (11) | 0·0552 (10) | 0·3603 (4) | 0·0395 |
| C(2) | 0·5273 (12) | 0·2459 (11) | 0·3047 (5) | 0·0496 |
| C(3) | 0·3262 (16) | 0·3752 (14) | 0·3153 (7) | 0·0717 |
| C(4) | 0·2046 (11) | 0·2649 (11) | 0·3841 (5) | 0·0479 |
| H(1)C2 | 0·648 | 0·324 | 0·324 | 0·057 |
| H(2)C2 | 0·547 | 0·206 | 0·245 | 0·116 |
| H(1)C3 | 0·248 | 0·378 | 0·262 | 0·144 |
| H(2)C3 | 0·359 | 0·517 | 0·333 | 0·101 |

† The *z* coordinate of the I atom is fixed to determine the origin along the fourfold axis.

When the above final parameters were introduced in space group $P4_3$, the calculation resulted in an *R* value of 0·079. When the enantiomer of the original molecule was treated in $P4_3$, the *R* value was 0·020, thus confirming the absolute configuration of the crystal to be $P4_1$ rather than the enantiomeric space group $P4_3$.

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* Preliminary X-ray examination of crystals of *N*-iodosuccinimide by Yardley (1925) and Tutton (1925) gave an axial ratio *a*:*c* of 1:2·471 which is different from that of 1:0·8733 reported by Groth from Traube's (1894) original work. When the Groth cell was transformed to the X-ray unit cell, a ratio of 1:2·469 was obtained which is in agreement with the value obtained by Yardley and with the value obtained in the present work. The transformation matrix converting the Groth cell to that employed in X-ray work is [110/−110/004]. The X-ray studies by Yardley and optical activity measurements by Tutton had showed the crystals of *N*-iodosuccinimide to possess only axes but no planes or centers of symmetry and therefore to belong to the tetragonal pyramidal (point group 4) class.

* A table of anisotropic thermal parameters and a list of observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52155 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Atomic scattering factors from Cromer & Waber (1974), full-matrix least-squares refinement using *SHELX*76 (Sheldrick, 1976).

*Kundt–Bürker pyroelectric test.* A single crystal of *N*-iodosuccinimide was heated on a microscope slide to ~353 K for 5–10 min. The slide was removed from the hot stage, and after 3–5 s sprayed with a mixture of yellow flowers of sulfur, carmine and lycopodium powder dyed with methyl violet as described earlier (Patil, Curtin & Paul, 1985).

**Discussion.** Final atomic parameters are given in Table 1 and bond lengths, angles and torsion angles in Table 2. The atom-numbering scheme is shown in Fig. 1, and the crystal packing of the $P4_1$ structure and also that for the enantiomeric structure in space group $P4_3$ are illustrated in Fig. 2. Even though the individual molecules are approximately planar, individual crystals are both polar and chiral.* The crystal morphology for each of the two idealized enantiomeric crystals is shown in Fig. 3.

*Pyroelectric effect and calculation of the direction of the dipole moment.* The polar axis in the crystal of *N*-iodosuccinimide is the crystallographic *c* axis. Application of the Kundt–Bürker test (Patil, Curtin, & Paul, 1985) to crystals of *N*-iodosuccinimide with the morphology shown in Fig. 3 indicated that, on heating, the blunt end of the crystal became red-yellow (developed positive charge) and the sharp end blue (developed negative charge).† It has been found in several other cases (Pennington *et al.*, 1988, and references therein; Padmanabhan, Paul & Curtin, in preparation), that the direction of the electric dipole developed on heating the crystal (pyroelectric effect) is the same as the direction of polarization of the crystal resulting from the orientation of its internal structure. If this is assumed then the orientations of molecules in the crystals in Fig. 3 can be deduced if the direction of the dipole moment of the individual molecules in the crystal is known. It is necessary, then, to find the dipole moments of individual molecules in their orientation in Fig. 2 and, in particular the component of this moment along the polar *c* crystal axis.

Table 2. *Bond lengths* (Å), *angles* (°) *and torsion angles* (°) *for N-iodosuccinimide*

| | | | |
|---|---|---|---|
| I—N | 2·059 (6) | O(1)—C(1) | 1·225 (8) |
| N—C(1) | 1·366 (8) | C(1)—C(2) | 1·499 (9) |
| C(2)—C(3) | 1·524 (11) | O(2)—C(4) | 1·216 (9) |
| N—C(4) | 1·396 (8) | C(3)—C(4) | 1·488 (11) |
| I—N—C(1) | 124·6 (4) | I—N—C(4) | 123·4 (5) |
| C(1)—N—C(4) | 112·0 (6) | O(1)—C(1)—N | 122·1 (6) |
| O(1)—C(1)—C(2) | 128·7 (7) | N—C(1)—C(2) | 109·2 (6) |
| C(1)—C(2)—C(3) | 104·5 (6) | C(2)—C(3)—C(4) | 104·9 (6) |
| O(2)—C(4)—N | 123·0 (7) | O(2)—C(4)—C(3) | 128·3 (7) |
| N—C(4)—C(3) | 108·7 (6) | | |
| N—C(1)—C(2)—C(3) | −7.9 (8) | C(2)—C(1)—N—I | −175·4 (4) |
| C(1)—C(2)—C(3)—C(4) | 7·1 (8) | C(3)—C(4)—N—I | −179·8 (5) |
| C(2)—C(3)—C(4)—N | −4·2 (9) | C(3)—C(2)—C(1)—O(1) | 173·9 (7) |
| C(3)—C(4)—N—C(1) | −0·8 (8) | C(2)—C(3)—C(4)—O(2) | 176·7 (8) |
| C(4)—N—C(1)—C(2) | 5·6 (8) | | |

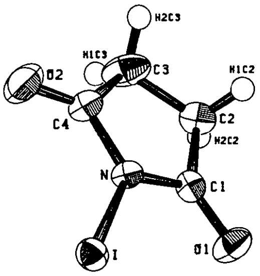

Fig. 1. A molecule of *N*-iodosuccinimide showing the numbering system employed here.

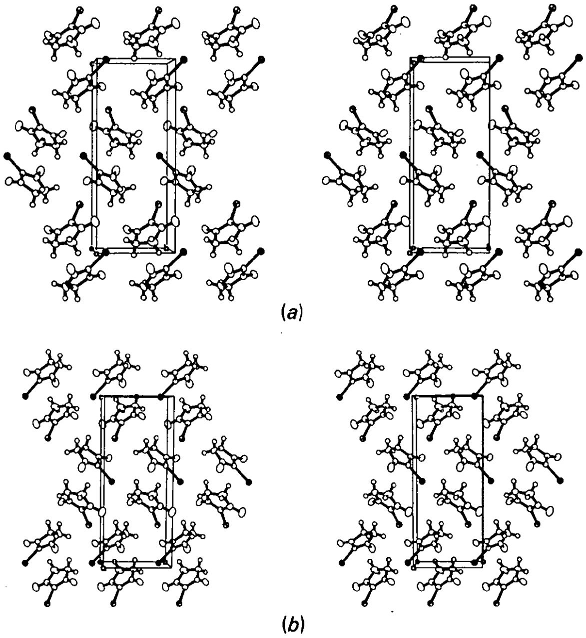

Fig. 2. (*a*) Crystal packing of $P4_1$ *N*-iodosuccinimide. Note that the polar *c* axis is vertical in the plane of the page pointing upward. The I atoms are directed toward the faces at the +*c* end of the crytal. (*b*) Crystal packing of the hypothetical enantiomer, $P4_3$ *N*-iodosuccinimide. The axial orientation is the same as in (*a*). In this case the directions of the nitrogen—iodine bonds are reversed with respect to the polar *c* axis.

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* As indicated in the *Experimental* section the crystal employed for the structure determination reported here was shown to belong to space group $P4_1$ and so to have the absolute configuration shown rather than that of the enantiomeric crystal in space group $P4_3$. Unfortunately, its chirality is preserved only in the crystal since this compound is achiral in solution.

† This result is opposite to the direction previously reported (Traube, 1894). The absolute configurations of the crystals to which the test was applied were unknown but it will be noted that in going from the (+) to the (−) crystal both the molecular orientation along *c* and the faces at the two ends of the polar axis are reversed so the argument here does not depend on the absolute configuration of the crystal.

Table 3. *Intermolecular interaction parameters* (Å *and* °) *involving oxygen* (O) *and halogen* (*Hal*) *for N-iodosuccinimide, N,N-diiodoformamide, N-bromosuccinimide and N-chlorosuccinimide*

| | Space group | O···*Hal** | C=O···*Hal* | N-*Hal*···O | Reference |
|---|---|---|---|---|---|
| *N*-Iodosuccinimide | $P4_1$ | 2·580 (6) | 121·6 (5) | 175·7 (2) | Present work |
| *N*,*N*-Diiodoformamide | $Pn2_1a$ | 2·565 (7) | 122·5 (6) | 171·3 (4) | Pritzkow (1974) |
| | | 3·130 (8) | 147·3 (6) | 150·9 (3) | Pritzkow (1974) |
| *N*-Bromosuccinimide | $P2_12_12_1$ | 2·802 (7) | 140·9 (6) | 169·5 (3) | Jabay *et al.*, (1977) |
| *N*-Chlorosuccinimide | $P2_12_12_1$ | 2·880 | 136·5 | 168·9 | Brown (1961) |

* van der Waals sums: O···I = 3·50, O···Br = 3·35, O···Cl = 3·20 Å.

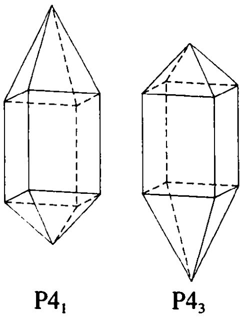

Fig. 3. Idealized crystal morphology showing the principal faces of the two iodosuccinimide enantiomers with the polar *c* axis oriented as in Fig. 2. [The left-hand drawing is similar to that published by Groth (1910).] The pyroelectric effect shows that on heating of the $P4_1$ crystal the pointed end, made up of faces of form {101}, develops negative charge while the blunt end, form $\{10\bar{2}\}$ becomes positively charged. The center faces are {100}. Although the crystal morphology differentiates the ends of the polar axis it does not permit enantiomeric crystals to be distinguished from one another.

The molecular dipole moment was calculated using the coordinates obtained from X-ray data together with the program *AM*1 of the *AMPAC* semi-empirical molecular orbital package developed by Dewar, Zoebisch, Healy & Stewart (1985). The molecular moment was found to be 2·37 debye (7·91 $\times 10^{-30}$ C m) with the direction approximately along the N—I bond and with the negative end of the dipole toward the I atom. The dipole vector was oriented at an angle of 128° with the polar *c* axis resulting in a component of 1·47 debye (4·90 $\times 10^{-30}$ C m) along the polar axis. It follows that for the $P4_1$ enantiomer the polarization of the $+c$ end of the crystal is electrically negative and the $-c$ end positive. Putting these results together with crystal packing drawings in Fig. 2 and the crystal morphologies shown in Fig. 3 it is found that in the $P4_1$ structure the 'sharp' end of the crystal is oriented toward the (+) end of the *c* crystallographic axis whereas in the $P4_3$ crystal the 'blunt' end of the crystal is toward $+c$.

The dipole moment of *N*-iodosuccinimide has been measured in dioxane solution (Lumbroso, Gasco & Malen, 1951) and the value reported is 0·97 debye ($3{\cdot}24 \times 10^{-30}$ C m) at 293 K. The large discrepancy between the measured value and the one calculated on the basis of the molecular geometry from the X-ray structure [2·37 debye ($7{\cdot}912 \times 10^{-30}$ C m)] may be due in part to interaction of iodosuccinimide molecules with the dioxane solvent.

*Molecular structure.* Although *N*-iodosuccinimide has a nearly planar skeleton and is achiral in a fluid medium, the molecules are chiral in the crystal, due primarily to the twisting of the five-membered ring; the torsion angle of C atoms C(1)—C(2)—C(3)—C(4) is 7·1 (8)°. Interestingly *N*-chlorosuccinimide (Brown, 1961) and *N*-bromosuccinimide (Jabay, Pritzkow, & Jander, 1977) both crystallize as chiral molecules in a space group ($P2_12_12_1$) which is chiral but not polar. Of particular interest in this regard is *N*-chlorophthalimide (2) (Groth, 1917) which belongs to point group 222 and crystallizes from acetone in the form of crystals whose chiral morphology distinguishes the two enantiomeric crystals from each other.

The bond lengths and angles of *N*-iodosuccinimide, except those of the N—halogen bond, agree with the corresponding values in *N*-bromosuccinimide (Jabay, Pritzkow & Jander, 1977) within experimental error. The N—I bond length in *N*-iodosuccinimide [2·059 (6) Å] lies between those of the two N—I bonds [2·041 (8) and 2·100 (7) Å] reported for the structure of *N*,*N*-diiodoformamide (Pritzkow, 1974).

An interesting feature of the crystal structure of *N*-iodosuccinimide is the short intermolecular O···I contacts. The intermolecular O(1)···I distance is found to be 2·580 (6) Å which is much shorter than the O···I van der Waals sum of 3·50 Å. Such O···halogen interactions have been observed in many other structures and have been analyzed in some detail (see Hassel & Romming, 1962, 1967; Leser & Rabinovich, 1978; Cody & Murray-Rust, 1984; Murray-Rust & Motherwell, 1979; Ramasubbu, Parthasarathy & Murray-Rust, 1986). These O···I interactions link the molecules to form zig-zag chains (Fig. 2). The intermolecular angles are C(1)=O(1)···I = 121·6 (5) and N—I···O(1) = 175·7 (2)°, close to the ideal geometry (C=O···I = 120 and *R*—I···O = 180°) which has been proposed for this type of association. Similar interactions have been reported for the structure of *N*,*N*-

diiodoformamide (Pritzkow, 1974). The various parameters are given in Table 3. Of the two short O···I contacts in *N*,*N*-diiodoformamide, one is very similar to that in *N*-iodosuccinimide and the other one weaker. The crystal structures of *N*-chloro- and *N*-bromosuccinimide display similar features. Intermolecular O···Cl and O···Br distances (2·88 and 2·80 Å) in these structures are shorter than the van der Waals sums of 3·20 and 3·35 Å respectively (Brown, 1961; Jabay, Pritzkow & Jander, 1977).*

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* A referee has noted that C—H···O contacts might be as important (Desiraju, 1987; Murray-Rust & Glusker, 1984) as the I···O contacts discussed here. Thus there is a short O(2)···H(2)—C(2) distance of 2·45 Å between an oxygen of one molecule and a methylene group of the molecule produced by the $4_1$ operation. The C—O···H angle is 155°.

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# The Structures of the Isostructural Adducts Triphenylphosphine Oxide–Trifluoroborane and Triphenylarsine Oxide–Trifluoroborane

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**Abstract.** $C_{18}H_{15}OP.BF_3$, $M_r$ = 346·09, monoclinic, $P2_1/n$, $a$ = 9·427 (3), $b$ = 18·043 (2), $c$ = 10·089 (2) Å, $\beta$ = 104·24 (2)°, $V$ = 1663·3 Å$^3$, $Z$ = 4, $D_x$ = 1·382 Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·70926 Å, $\mu$ = 0·205 mm$^{-1}$, $F$(000) = 712, $T$ = 293 K, $R$ = 0·035 for 1185 significant reflections. $C_{18}H_{15}AsO.BF_3$, $M_r$ = 390·0, monoclinic, $P2_1/n$, $a$ = 9·520 (2), $b$ = 18·231 (3), $c$ = 10·142 (2) Å, $\beta$ = 104·21 (2)°, $V$ = 1706·3 Å$^3$, $Z$ = 4, $D_x$ = 1·518 Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·70926 Å, $\mu$ = 2·14 mm$^{-1}$, $F$(000) = 784, $T$ = 293 K, $R$ = 0·0281 for 1982 reflections. The structures consist of discrete molecular units and are isostructural. The angles at oxygen [P—O—B = 134·5 (2), As—O—B = 125·7 (2)°] and the $E$—O ($E$ = P, As) bond lengths [P—O = 1·522 (3) Å, As—O = 1·690 (3) Å] are typical for related adducts and allow a useful comparison of the adduct effect on the $E$—O $\pi$ character.

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