

Synthesis and structure of bis(4-iodophenoxy)triphenylantimony and 4-iodophenoxytetraphenylantimony

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A reaction of triphenylantimony with 4-iodophenol in the presence of hydrogen peroxide furnished bis(4-iodophenoxy)triphenylantimony, which when treated with pentaphenylantimony gave 4-iodophenoxytetraphenylantimony. The structure of organoantimony compounds was studied by ^1H and ^{13}C NMR spectroscopy and X-ray crystallography.

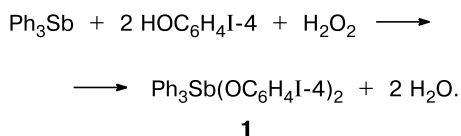
Key words: triphenylantimony, hydrogen peroxide, 4-iodophenol, pentaphenylantimony, bis-(4-iodophenoxy)triphenylantimony, 4-iodophenoxytetraphenylantimony, synthesis, structure.

Earlier, we have shown that antimony derivatives of general formula Ph_4SbX (X is an electronegative substituent) can be obtained from pentaphenylantimony and HX (X = OR,¹ OAr,² OC(O)R,³ OSO₂R,⁴ ON=CRR'⁵). No less efficient method for the synthesis of the indicated derivatives is the reaction of pentaphenylantimony and antimony derivatives of general formula Ph_3SbX_2 , in these cases the target product has been isolated in almost quantitative yield.⁶ Note that the synthesis of tetraphenylantimony aroxides by the ligand exchange reaction is described in the only work.⁷

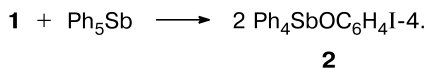
The interest to the indicated issue is due to the biological activity of some pentavalent antimony organic derivatives.^{8–10}

The purpose of the present work is the synthesis of two new antimony compounds: bis(4-iodophenoxy)triphenylantimony (**1**) and 4-iodophenoxytetraphenylantimony (**2**).

Compound **1** was synthesized by the oxidative addition reaction¹¹ from triphenylantimony, 4-iodophenol, and hydrogen peroxide in diethyl ether at 20 °C:



It was found that compound **1** reacted with pentaphenylantimony in toluene with the formation of 4-iodophenoxytetraphenylantimony (**2**) in 76% yield:



This method for the synthesis of **2** applied to compounds of general formula Ph_4SbX is very promising

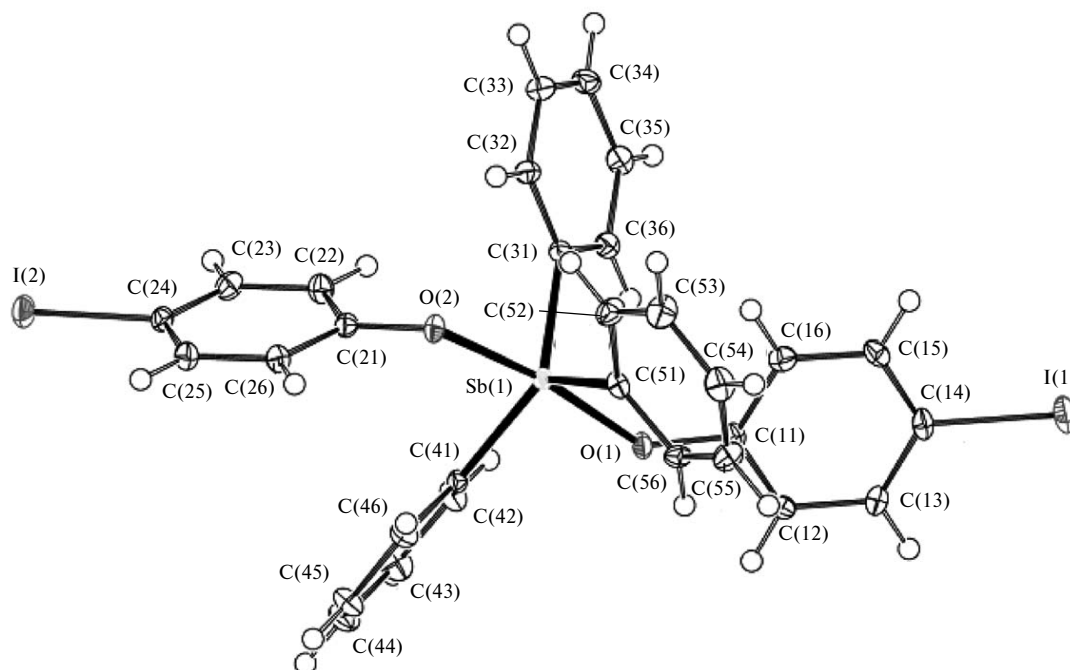
because it gives high yield the final product, the amount of which reaches two moles calculated on one mole of the starting pentaphenylantimony.¹¹

The structures of the synthesized compounds **1** and **2** were established based on the analysis of ^1H and ^{13}C NMR spectroscopy data and X-ray crystallography.

^1H NMR spectra of compounds **1** and **2** exhibit doublets for the protons of the aroxy groups with the ratio of integral intensities of 1 : 1, which are significantly upfield shifted as compared to the signals for the protons of the phenyl groups. Such a tendency is also observed in the ^{13}C NMR spectra, in which the signals for the carbon atoms of the aroxy groups in compounds **1** and **2** are observed in the region of δ 76.697–79.745 and 76.639–77.364, respectively, whereas the signals for the carbon atoms of the phenyl groups are found in the region of δ 122.48–137.58 and 123.01–137.02, respectively.

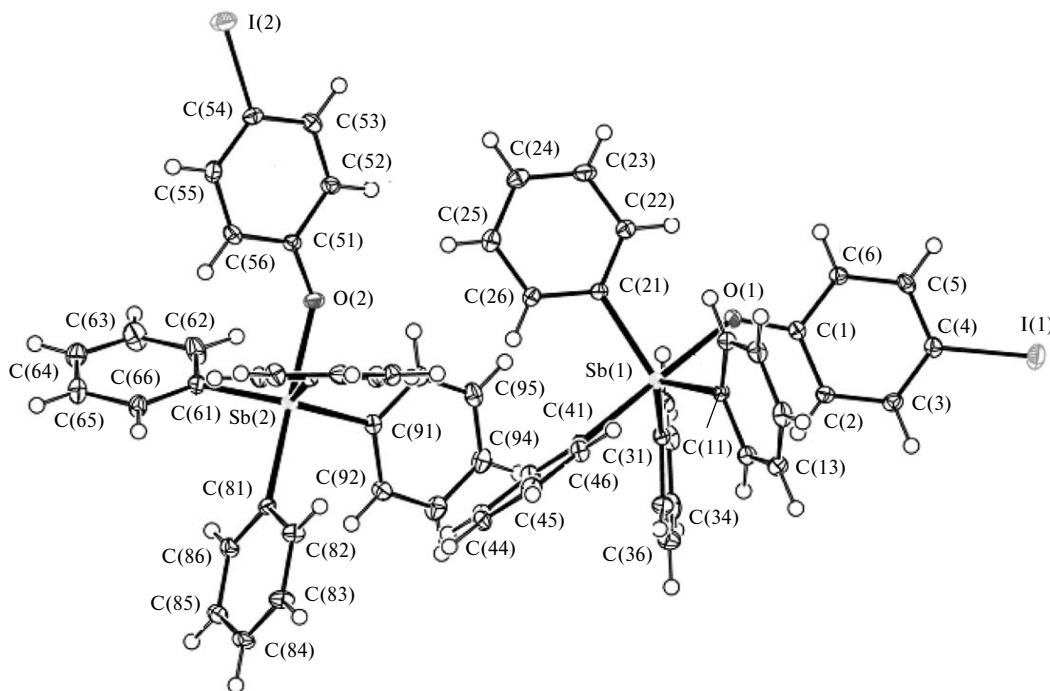
X-ray diffraction studies of compounds **1** and **2** showed that the antimony atoms have a distorted trigonal bipyramidal coordination, with the oxygen atoms of the aroxy ligands occupying the axial positions (Figs 1 and 2). In crystal **2**, two types of crystallographically independent molecules are present (*a*, *b*).

The axial angles OSbO and OSbC are equal to 172.15(8)° (**1**) and 177.83(8)° (**2A**), 178.58(8)° (**2B**). The sums of the angles CSbC in the equatorial plane are 360° (**1**) and 358.08° (**2A**), 357.48° (**2B**). In crystal **1**, the antimony atom lies virtually in the equatorial plane (the deviation is 0.008 Å), in **2A** and **2B** the central atom deviates from the plane C₃ to the side of axial carbon atom by 0.170 and 0.162 Å, respectively, which indicates a distortion of the trigonal bipyramidal configuration of the molecules. Molecules **1** and **2** differ in conformation of the phenyl rings relative to the equatorial plane. Thus, in crystal **1** the planes

**Fig. 1.** Molecular structure of **1**.

C(31)—C(36), C(41)—C(46), and C(51)—C(56) have the following angles with the equatorial plane: 61.17° , 37.52° , and 50.94° , respectively. In crystal **2A**, one of the phenyl rings is virtually perpendicular to the equatorial plane (the corresponding angle is equal to 81.88°), whereas the plane of the other phenyl ring has the angle of 18.71° with the equat-

orial plane, the third phenyl ring is arranged relative to the equatorial plane at the angle of 43.49° . In crystal **2B**, similar angles are 77.52° , 15.65° , and 43.93° . In crystal **1**, the planes of the aroxy groups C(11)—C(16) and C(21)—C(26) have the angles of 80.27° and 51.37° with the equatorial plane, in crystals **2A** and **2B** similar angles are 76.59° and 77.17° .

**Fig. 2.** Molecular structure of **2**.

The equatorial bonds Sb—C in crystal **1** are equal within the experiment error limits (2.103(3), 2.104(3), 2.105(2) Å) and are shorter than in crystals **2A** (2.115(3)—2.128(3) Å) and **2B** (2.113(3)—2.124(3) Å). The length of the axial bonds Sb—C in **2A** and **2B** is 2.195(3) and 2.193(3) Å, respectively. Note that the Sb—O bond distances in compound **2** (2.1618(19) (A) and 2.1644(19) Å (B)) are comparable with similar distances in the antimony aroxy-tetraphenyl compounds (*cf.* Ref. 12: 2.132(6)—2.221(4) Å), but are considerably longer than the Sb—O bond distances (2.0687(17) and 2.0657(16) Å) in compound **1**, whose values approximate the sum of the covalent radii of O and Sb atoms equal to 2.07 Å (see Ref. 13).

Experimental

IR spectra of compounds **1** and **2** were recorded on a Bruker Tensor 27 IR spectrometer in KBr pellets in the region of 4000—400 cm^{−1}.

¹H and ¹³C NMR spectra were recorded on an Agilent DD2 400 spectrometer (400 MHz) in CDCl₃, using HMDS as an internal standard (for ¹H) and signal of the solvent as a reference (for ¹³C).

Elemental analysis was performed on a Carlo Erba CHNS-O EA 1108 elemental analyzer. Melting points of compounds **1** and **2** were measured on a Stuart SMP 30 appliance.

X-ray diffraction studies of crystals **1** and **2** were performed on a Bruker-Nonius X8Apex diffractometer (Mo-K α radiation, λ = 0.71073 Å, graphite monochromator). Collection and processing of data and refinement of unit cell parameters, as well as correction for absorption were performed using the SMART and SAINT-Plus¹⁴ programs. All the calculations on solution and refinement of the structures were performed using the SHELXL/PC¹⁵ programs. The structures were solved by direct method and refined by the least squares method in anisotropic approximation for nonhydrogen atoms. The main crystallographic data and results of the structure refinement are given in Table 1, principal bond distances and bond angles are summarized in Table 2.

The full Tables of atomic coordinates, bond distances and bond angles were deposited with the Cambridge Crystallographic

Table 1. Crystallographic data, parameters of experiment and refinement for structures **1** and **2**

| Parameter | Value | |
|---|--|--|
| | 1 | 2 |
| M | 791.03 | 649.14 |
| T/K | 100.15 | 100.15 |
| Crystal system | Monoclinic | Triclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> $\bar{1}$ |
| <i>a</i> /Å | 15.4189(8) | 10.7650(4) |
| <i>b</i> /Å | 8.9576(5) | 13.3173(6) |
| <i>c</i> /Å | 20.8616(10) | 17.5920(8) |
| α /deg | 90.00 | 95.7570(10) |
| β /deg | 110.6680(10) | 90.6120(10) |
| γ /deg | 90.00 | 98.8940(10) |
| <i>V</i> /Å ³ | 2695.9(2) | 2478.23(18) |
| <i>Z</i> | 4 | 4 |
| ρ_{calc} /g cm ^{−3} | 1.949 | 1.740 |
| μ /mm ^{−1} | 3.339 | 2.380 |
| <i>F</i> (000) | 1504.0 | 1264.0 |
| Crystal size/mm | 0.222×0.219×0.06 | 0.199×0.141×0.124 |
| θ range of data collection/deg | 4.14—76.52 | 3.12—72.98 |
| Reflection collected | −26 ≤ <i>h</i> ≤ 25, −8 ≤ <i>k</i> ≤ 14, −35 ≤ <i>l</i> ≤ 26 | −17 ≤ <i>h</i> ≤ 17, −21 ≤ <i>k</i> ≤ 22, −2 ≤ <i>l</i> ≤ 27 |
| Reflection collected | 21916 | 28053 |
| Independent reflections | 13040 | 22320 |
| (<i>R</i> _{int}) | (0.0312) | (0.0226) |
| Refinement variables | 316 | 603 |
| GOOF | 1.000 | 0.999 |
| <i>R</i> -factors on $F^2 > 2\sigma(F^2)$ | | |
| <i>R</i> ₁ | 0.0390 | 0.0416 |
| <i>wR</i> ₂ | 0.0685 | 0.0751 |
| <i>R</i> -factors on all reflections | | |
| <i>R</i> ₁ | 0.0653 | 0.0693 |
| <i>wR</i> ₂ | 0.0774 | 0.0854 |
| Residual electron density | 1.44/−1.59 | 1.37/−1.86 |
| (min/max)/e Å ^{−3} | | |

Table 2. Principal bond distances and bond angles in the structures **1** and **2**

| Bond | <i>d</i> /Å | Angle | ω /deg |
|-------------------|-------------|-------------------|---------------|
| Molecule 1 | | | |
| Sb(1)—O(1) | 2.0687(17) | O(1)—Sb(1)—C(31) | 94.93(8) |
| Sb(1)—O(2) | 2.0657(16) | O(1)—Sb(1)—C(41) | 83.19(8) |
| Sb(1)—C(31) | 2.103(3) | O(1)—Sb(1)—C(51) | 93.43(8) |
| Sb(1)—C(41) | 2.105(2) | O(2)—Sb(1)—O(1) | 172.15(8) |
| Sb(1)—C(51) | 2.104(3) | O(2)—Sb(1)—C(31) | 91.94(9) |
| O(1)—C(11) | 1.355(3) | O(2)—Sb(1)—C(41) | 89.96(8) |
| O(2)—C(21) | 1.361(3) | O(2)—Sb(1)—C(51) | 87.59(8) |
| I(1)—C(14) | 2.101(2) | C(31)—Sb(1)—C(41) | 121.90(10) |
| I(2)—C(24) | 2.097(2) | C(31)—Sb(1)—C(51) | 111.39(10) |
| C(11)—C(12) | 1.396(4) | C(51)—Sb(1)—C(41) | 126.70(10) |
| C(11)—C(16) | 1.400(4) | C(11)—O(1)—Sb(1) | 133.28(16) |
| C(12)—C(13) | 1.387(3) | C(21)—O(2)—Sb(1) | 124.58(15) |
| Molecule 2 | | | |
| Sb(1)—O(1) | 2.1618(19) | O(1)—Sb(1)—C(41) | 177.83(8) |
| Sb(1)—C(41) | 2.195(3) | C(31)—Sb(1)—O(1) | 85.64(9) |
| Sb(1)—C(31) | 2.115(3) | C(31)—Sb(1)—C(41) | 96.00(10) |
| ×Sb(1)—C(21) | 2.128(3) | C(31)—Sb(1)—C(21) | 116.15(10) |
| Sb(1)—C(11) | 2.118(2) | C(31)—Sb(1)—C(11) | 124.76(10) |
| I(1)—C(4) | 2.102(3) | C(21)—Sb(1)—O(1) | 83.57(9) |
| Sb(2)—O(2) | 2.1644(19) | C(21)—Sb(1)—C(41) | 96.95(10) |
| Sb(2)—C(71) | 2.113(3) | C(11)—Sb(1)—O(1) | 86.80(9) |
| Sb(2)—C(91) | 2.124(3) | C(11)—Sb(1)—C(41) | 91.09(10) |
| Sb(2)—C(81) | 2.193(3) | C(11)—Sb(1)—C(21) | 117.17(10) |
| Sb(2)—C(61) | 2.122(3) | O(2)—Sb(2)—C(81) | 178.58(8) |
| I(2)—C(54) | 2.104(3) | C(71)—Sb(2)—O(2) | 87.76(9) |
| O(1)—C(1) | 1.337(3) | C(71)—Sb(2)—C(91) | 116.57(10) |
| O(2)—C(51) | 1.330(3) | C(71)—Sb(2)—C(81) | 91.38(10) |
| C(15)—C(16) | 1.392(4) | C(71)—Sb(2)—C(61) | 123.74(10) |
| C(15)—C(14) | 1.382(4) | C(91)—Sb(2)—O(2) | 82.91(9) |
| C(71)—C(72) | 1.394(4) | C(91)—Sb(2)—C(81) | 96.48(10) |
| C(71)—C(76) | 1.395(4) | C(61)—Sb(2)—O(2) | 86.00(9) |
| C(41)—C(46) | 1.398(4) | C(61)—Sb(2)—C(91) | 117.95(10) |
| C(41)—C(42) | 1.405(4) | C(61)—Sb(2)—C(81) | 95.42(10) |
| C(91)—C(92) | 1.403(4) | C(1)—O(1)—Sb(1) | 131.23(16) |
| C(91)—C(96) | 1.395(4) | C(51)—O(2)—Sb(2) | 131.76(18) |

Data Center: CCDC 998314 for **1** and CCDC 998315 for **2** (deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).

Bis(4-iodophenoxy)triphenylantimony (1). A 30% aqueous solution of hydrogen peroxide (160 mg) was added to a mixture of triphenylantimony (500 mg, 1.42 mmol) and 4-iodophenol (623 mg, 2.82 mmol) in diethyl ether (20 mL) and the mixture was allowed to stand for 24 h at 20 °C. Colorless crystals formed were filtered and dried. The yield was 1020 mg (91%). M.p. 184 °C. IR, ν/cm^{-1} : 3091, 3067, 2925, 2854, 1567, 1274, 1243, 1169, 1098, 1069, 1022, 997, 829, 822, 743, 730, 693, 645, 635, 617, 534, 519, 592, 480, 459. ^1H NMR, δ : 6.10 (d, 4 H, Ar, $J = 8.72$ Hz); 7.11 (d, 4 H, Ar, $J = 8.71$ Hz); 7.46 (m, 9 H, $p\text{-H}_{\text{Ph}}$, $m\text{-H}_{\text{Ph}}$); 8.04 (m, 6 H, $o\text{-H}_{\text{Ph}}$). ^{13}C NMR, δ : 76.70–79.75 (Ar); 122.48–137.58 (Ph). Found (%): C, 45.38; H, 3.08. $\text{C}_{30}\text{H}_{23}\text{O}_2\text{I}_2\text{Sb}$. Calculated (%): C, 45.54; H, 2.91.

4-Iodophenoxytetraphenylantimony (2). A mixture of bis-(4-iodophenoxy)triphenylantimony (0.395 mg, 0.50 mmol) and pentaphenylantimony (253 mg, 0.50 mmol) in benzene (5 mL)

was heated for 1 h at 80 °C. The reaction mixture was concentrated to 0.5 mL and cooled to 10 °C. Crystals formed were filtered, washed with hexane (5 mL) and dried. The yield was 571 mg (88%). M.p. 162 °C. IR, ν/cm^{-1} : 3091, 3067, 3058, 3047, 3014, 2925, 2854, 1567, 1475, 1433, 1283, 1169, 1062, 997, 839, 822, 800, 729, 692, 634, 607, 511, 491, 464, 452. ^1H NMR, δ : 5.83 (d, 2 H, Ar, $J = 8.74$ Hz); 6.95 (d, 2 H, Ar, $J = 8.74$ Hz); 7.26–7.45 (m, 12 H, $p\text{-H}_{\text{Ph}}$, $m\text{-H}_{\text{Ph}}$); 7.68 (d, 8 H, $o\text{-H}_{\text{Ph}}$). Found (%): C, 55.36; H, 3.81. $\text{C}_{30}\text{H}_{24}\text{OISb}$. Calculated (%): C, 55.50; H, 3.70.

References

- G. A. Razuvaev, N. A. Osanova, T. G. Brilkina, T. I. Zinovjeva, V. V. Sharutin, *J. Organomet. Chem.*, 1975, **99**, 93.
- V. V. Sharutin, V. V. Zhidkov, D. V. Muslin, N. S. Lyapina, G. K. Fukin, L. N. Zakharov, A. I. Yanovskii, Yu. T. Struch-

- kov, *Russ. Chem. Bull. (Engl. Transl.)*, 1995, **44**, 931 [*Izv. Akad. Nauk, Ser. Khim.*, 1995, 958].
3. V. V. Sharutin, O. K. Sharutina, A. P. Pakusina, V. K. Bel'sky, *J. Organomet. Chem.*, 1997, **536**, 87.
4. V. V. Sharutin, O. K. Sharutina, L. P. Panova, V. K. Bel'sky, *Russ. J. Gen. Chem. (Engl. Transl.)*, 1997, **67**, 1438 [*Zh. Obshch. Khim.*, 1997, **67**, 1528].
5. V. V. Sharutin, O. K. Sharutina, O. V. Molokova, E. N. Ettenko, D. B. Krivolapov, A. T. Gubaidullin, I. A. Litvinov, *Russ. J. Gen. Chem. (Engl. Transl.)*, 2001, **71**, 1243 [*Zh. Obshch. Khim.*, 2001, **71**, 1317].
6. V. V. Sharutin, V. S. Senchurin, O. K. Sharutina, A. P. Pakusina, L. P. Panova, *Russ. J. Gen. Chem. (Engl. Transl.)*, 1996, **66**, 1710 [*Zh. Obshch. Khim.*, 1996, **66**, 1755].
7. V. V. Sharutin, O. K. Sharutina, P. E. Osipov, O. V. Subacheva, *Russ. J. Gen. Chem. (Engl. Transl.)*, 2001, **71**, 983 [*Zh. Obshch. Khim.*, 2001, **71**, 1045].
8. E. R. T. Tiekink, *Crit. Rev. Oncol./Hematol.* 2002, **42**, 217.
9. I. I. Ozturk, C. N. Banti, M. J. Manos, A. J. Tasiopoulos, N. Kourkoumelis, K. Charalabopoulos, S. K. Hadjikakou, *J. Inorg. Biochem.*, 2012, **109**, 57.
10. M. I. Ali, M. K. Rauf, A. Badshah, I. Kumar, C. M. Forsyth, P. C. Junk, L. Kedzierski, P. C. Andrews, *Dalton Trans.*, 2013, **42**, 16733.
11. V. V. Sharutin, V. S. Senchurin, *Imennye reaktsii v khimii elementoorganicheskikh soedinenii* [Named Reactions in Chemistry of Organoelement Compounds], Izdatel'skii Tsentr YuUrGU, Chelyabinsk, 2011, 427 pp. (in Russian).
12. O. K. Sharutina, V. V. Sharutin, *Molekulyarnye struktury organicheskikh soedinenii surmy(v)* [Molecular Structures of Antimony(v) Organic Compounds], Izdatel'skii Tsentr YuUrGU, Chelyabinsk, 2012, 395 pp. (in Russian).
13. S. S. Batsanov, *Zh. Inorg. Khim.*, 1991, **36**, 3015 [*J. Inorg. Chem. USSR (Engl. Transl.)*, 1991, **36**].
14. Bruker (1998). *SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System.* Bruker AXS Inc., Madison, Wisconsin, USA.
15. Bruker (1998). *SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data.* Bruker AXS Inc., Madison, Wisconsin, USA.

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