

Novel Enantiopure Bis(pyrrolo)tetrathiafulvalene Donors Exhibiting Chiral Crystal Packing Arrangements.

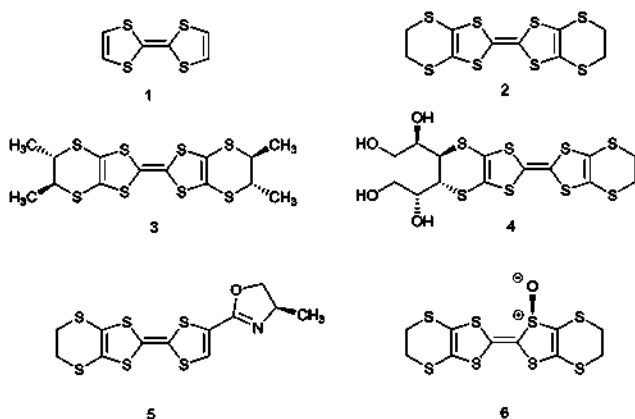
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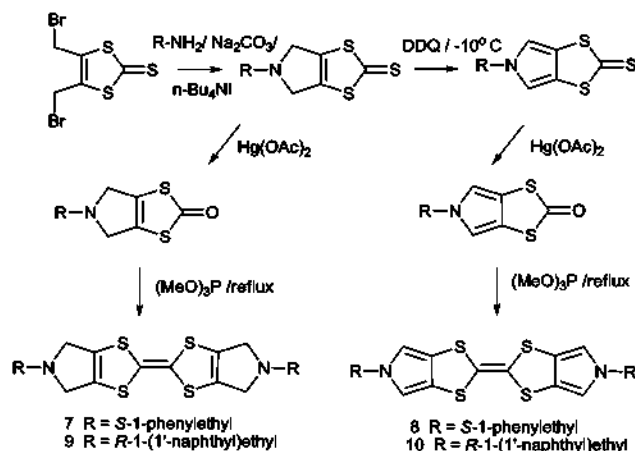
Two novel enantiopure bis(pyrrolo[3,4-d]tetrathiafulvalene derivatives, substrates for preparing chiral conducting materials, show chiral crystal packing arrangements in which successive layers are rotated in accordance with an exact or approximate 4₃ axis. The corresponding donors containing fused dihydropyrrole groups, and thus four more hydrogen atoms, form stacks along a crystal axis.



The influence of chirality on the electrical properties of materials has been a topic of discussion for many years,¹ and Rikken has recently proposed and demonstrated the phenomenon of electrical magnetochiral anisotropy in carbon nanotubes.² Radical cation salts of donors such as TTF 1 and BEDT-TTF 2 provide a family of materials for investigating this phenomenon if chirality can be incorporated in the system. A range of enantiopure or enantioenriched donors related to 2 with stereogenic centres at carbon³ or sulfur⁴ e.g. 3-6 have been prepared, but to date no radical cation salts with significant differences in packing arrangements between enantiomers have been prepared, due to the strong tendency of these donor molecules to pack face-to-face and often related by pseudo-centrosymmetry. Two comparisons of racemic and enantiopure salts, though, have been described.⁵ Salts with an enantiopure chiral anion⁶ or solvent molecule⁷ have also been studied. Day has demonstrated how the organization of the Δ and Λ enantiomers of chromium(III) tris(oxalate) influences the electrical properties of polymorphs of racemic $\text{ET}_4[(\text{H}_3\text{O})\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{CN}$ ⁸ and Martin has prepared the first conducting salt containing a single enantiomer in the series $\text{ET}_3(\text{X}^+) \Delta\text{-M}(\text{III})(\text{C}_2\text{O}_4)_3 \cdot \text{guest}$.⁹ Nevertheless, the preparation of chiral packing arrangements for the organosulfur donors has remained elusive,¹⁰ though helical systems containing TTF or β -fused thiophenes are emerging as potential systems for study.¹¹ Now we report four new enantiopure donors 7-10 based on the

bis(pyrrolo[3,4-d]tetrathiafulvalene system and the helical-type chiral packing arrangements of donors 8 and 10, an important stepping stone to the production of electroactive materials with chiral packing arrangements.

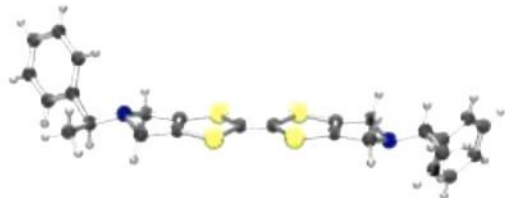
The preparative route (Scheme) builds on Becher's approach to bis(pyrrolo)TTF.^{12,13} The structures of the four donors 7-10 were measured by X-ray crystallography at 120 K.¹⁴ Donors 7



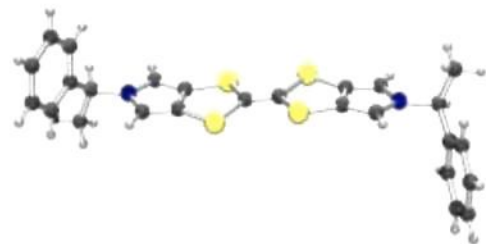
Scheme: Synthetic route to donors 7-10

and 9 containing dihydropyrrole rings form stacks in the crystal, while, remarkably, donors 8 and 10, containing just four less hydrogen atoms but with planar bonding geometry at nitrogen rather than pyramidal bonding geometry, form helical type crystal packing arrangements. Molecular structures are shown in Figure 1, with packing arrangements in Figures 2-5. Compared to the donors 7 and 9, the bond lengths in most parts of the pyrrole rings of 10 and 12 are notably shorter, e.g. C-N bonds, 1.358(6)-1.381(6) Å compared to 1.474(4)-1.495(8) Å and unfused C-C bonds 1.360(8)-1.373(6) Å compared to 1.481(9)-1.499(9) Å, while the bond at the ring fusion is longer 1.408(6)-1.417(6) Å compared to 1.336(7)-1.343(4) Å. Donor 8 which carries two 1-phenylethyl groups crystallises in the tetragonal space group $P4_32_12$ with four donor molecules in the unit cell which are related by the four fold screw axis along the c axis which is 42.205 Å long. Each donor is bisected by a two fold crystallographic axis in the plane of the donor system, so only half the donor is crystallographically unique. Donor 10 which differs from 8 by replacement of the phenyl rings with naphthyl rings, adopts a similar packing arrangement but in orthorhombic space group $C222_1$, with the a and b axes almost equal (10.8652(2) and 10.8969(2) Å) and with two independent donor

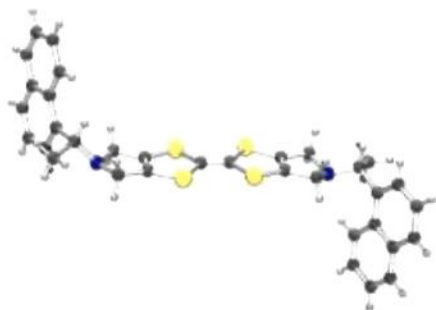
molecules, each of which is bisected by its own two fold crystallographic rotation axis along the *a* or *b* axis. There are four layers of donors lying perpendicular to the *c* axis, which are nearly related by a four fold screw axis. Thus, these two donors have axially chiral packing arrangements.



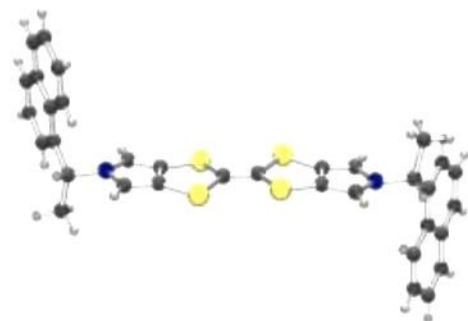
7



8



9



10

Figure 1: Molecular structures of donors 7-10¹⁴

The molecules of the phenyl substituted donor **8** are arranged in layers perpendicular to the *c* axis such that their bis(pyrrolo)TTF planes lie at 26.5° to the *ab* plane. Each S atom is involved in a close contact with a S atom of a neighbouring molecule in the layer (S...S 3.402(2) Å). The relative rotation of adjacent planes of molecules originates in the orientations of the phenyl groups. The conformation about the exocyclic N-C bond places the bond from the stereogenic centre to the methyl group almost perpendicular to the pyrrole plane so that the axis of the phenyl group makes torsion angles of 40.5° and -142.0° to the ring N-C bonds. The two phenyl groups are twisted so that their planes lie at 80° to exocyclic N-C bonds and are directed out from opposite faces of the donor molecule. It is the interlocking of phenylethyl groups between layers which controls the packing

arrangement (Fig 2). The donor molecules form layers in the *ab* plane, which leave grooves between lines of parallel phenyl groups, into which the phenyl groups from the layer above insert. The angle between the phenyl planes of interlocking layers is 36.6°. Inside the groove the *para* H atom of the benzene ring butts up against the pyrrole ring of a molecule in the next layer, with a H-C contact to an α -C atom of the pyrrole ring of 2.71 Å. The *para* C atom and one of the *meta* C atoms make contacts of 2.68 and 2.80 Å with the H atom from the stereogenic centre of a molecule in the next layer.

The molecular conformations and packing arrangement of donor **10** are very similar to those of donor **8**, except that there are two molecules which form independent layers perpendicular to the *c* axis, and that the stereogenic centres are displaced slightly (0.24-0.27 Å) from their pyrrole planes. The orientation of the aromatic ring is similar in both molecules, and close to that in donor **8**; the bond from the stereogenic centre to the naphthyl group makes torsion angles of -48.6 and 147.0 or -46.6 and 148.1° with the endocyclic N-C bonds, and the naphthyl rings are twisted to lie at 72 and 74° to the exocyclic N-C bonds. The planes of the bis(pyrrolo)TTF molecules lie *ca* 28° to the *ab* plane for both molecules. Within the two crystallographically unique layers molecules are related by the C centring, while the two

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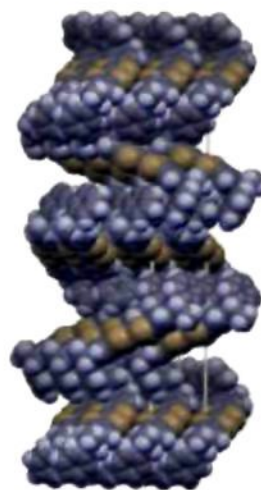


Figure 2. Packing of layers of **8** related by a 4₃ axis, viewed with *c* axis vertical.¹⁴

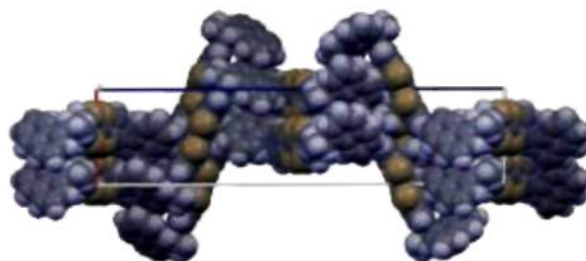


Figure 3. Crystal packing of **10** viewed along the *a* axis, with the *c* axis horizontal.¹⁴

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further layers perpendicular to *c* within the unit cell are generated by the 2₁ axis (Fig. 3). Within the two unique layers, the donor molecules makes short S...S contacts with other molecules from all four S atoms (S...S 3.5730(16) and 3.6456(16) Å) which indicate a slightly greater spacing than in the crystals of **8**. Following the pattern from **8**, the naphthyl groups of one layer slip into the grooves created by the naphthyl rings in the adjacent layer and lie at 26.1° to each other. The closest contacts at these interfaces are between the 5-H of the naphthyl system and a carbon at the fusion of pyrrole and dithiole rings (2.68 & 2.72 Å). *Trans, trans*-tetra(ethyl)BEDT-TTF has been reported to resolve on crystallization to give tetragonal crystals in P4₃2₁2, but the structure is not analogous to those described here.¹⁵

Donors **7** and **9**, contain pyramidal N atoms with each N atom lying 0.399-0.426 Å out of the plane of its three substituents. The conformation about the exocyclic N-C bonds places the H atom of the stereogenic centre roughly *anti* to the nitrogen lone pair in both molecules. In the phenyl substituted donor **7** both dihydropyrrole rings adopt envelope configurations with the N atoms lying *anti* to each other, 0.422 and -0.392 Å out of the best plane of their respective pyrrole ring carbon atoms. The chiral substituents adopt pseudo-equatorial



Figure 4: Crystal packing of donor **7** viewed down the *b* axis.¹⁴

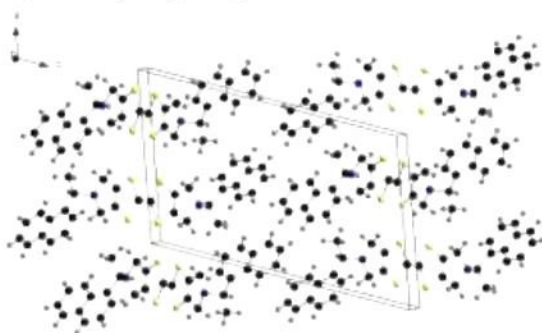


Figure 5: Crystal packing of donor **10** viewed down the *b* axis.¹⁴

positions so that neither stereogenic centre lies more than 0.11 Å out of the best plane of the TTF ring system. In contrast, in the naphthyl substituted donor **9** although both N atoms have pyramidal geometry, the dihydropyrrole ring conformations are different. One adopts a strong envelope conformation with the N atom lying 0.401 Å out of the plane of the pyrrole ring carbon atoms, with the chiral substituent taking up a pseudo-equatorial position and the naphthalene substituent oriented so its *peri* H atom makes a short contact with the ring N atom of just 2.46 Å. In contrast, the second dihydropyrrole ring is close to planar with the N atom lying just 0.080 Å out of the plane of the other four ring atoms, and the naphthalene is oriented with the *ortho* H atom, and not the *peri* H atom, near to the N atom (N...H 2.61

Å). The two stereogenic centres lie 0.175 and 1.108 Å to opposite sides of the best plane of the TTF system.

The chirality of the side chains has not forced these two donors to adopt helical-type packing arrangements. Donor **7** forms slipped stacks in the triclinic crystalline state (*Z*=1) with a spacing between TTF planes of 3.601 Å and the TTF groups oriented at 36° to the *a* stacking axis (Fig. 4). The shortest S...S contact between stacks is 3.707(2) Å. The planes formed by the stacks interface by contacts between benzene rings where the *para* H atom of one ring is directed towards the pi system of another ring. Donor **9** which crystallizes in space group P2₁ also forms similar slipped stacks, in this case along the *b* axis, but with neighbouring stacks related by 2₁ symmetry (Fig 5). The TTF planes lie at 35° the stacking axis and are 3.620 Å apart. There are close S...S contacts between the stacks of 3.417(2) and 3.468(2) Å involving all the sulfur atoms. The planes containing these stacks interface by making C-H/pi interactions involving the unsubstituted ring of the naphthyl groups with H...pi system separations of 2.68 and 3.08 Å.

Cyclic voltammetry measurements at a Pt electrode in 0.1 M *n*-Bu₄NPF₆ showed all donors to have two oxidation processes under 1 V (relative to Ag/AgCl), with the donors **7** and **9** showing slightly higher oxidation potentials than donors **8** and **10** (0.40-0.41 & 0.88-0.90 V *cf.* 0.36 & 0.86 V). The challenge now is to incorporate the crystal packing arrangements of donors **8** and **10** into their electroactive radical cation salts.

Notes and references

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[†] Electronic Supplementary Information (ESI) available: Experimental details for preparations. See DOI: 10.1039/b000000x/

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13. 7: m.p. 187-189°C (dec.); δ_H (CDCl₃): 7.26 (8H, m, 2\Ar-H₁), 7.19 (2H, m, 2\Ar-H₁), 3.64 (2H, q, J = 6.6 Hz, 2\CH), 3.53 (4H, m, 4-,4',-6-,6'-H₂), 3.43 (4H, m, 4-,4',-6-,6'-H₂), 1.32 (6H, d, J = 6.6 Hz, 2\CH₃); δ_C (CDCl₃): 144.4, 129.6, 128.6, 127.1 (2\Ar-C₆), 127.3 (3a-,3a'-,6a-,6a'-C), 117.4 (2-,2'-C), 65.2 (2\CHCH₃), 55.9 (4-,4',-6-,6'-C), 22.9 (2\CH₃); ν_{max} (ATR): 2973, 2885, 2789, 1489, 1450, 1367, 1322, 1305, 1278, 1206, 1178, 1158, 1135, 1078, 1058, 1028, 957, 902, 837, 759, 698, 548cm⁻¹; m/z : (EI) 494 [M]⁺; HRMS (EI) found: 494.0970, C₂₆H₂₆N₂S₄ requires: 494.0973; found C, 63.06; H, 5.38; N, 5.49%; C₂₆H₂₆N₂S₄ requires C, 63.12; H, 5.30; N, 5.66%; ²⁹³[α]_D = -44.5° (c = 0.2, CHCl₃); 8: m.p. 172-174°C; δ_H (CDCl₃): 7.23 (6H, m, 2\Ar-H₁), 7.04 (4H, m, 2\Ar-H₁), 6.45 (4H, s, 4-,4',-6-,6'-H), 5.12 (2H, br, 2\CHCH₃), 1.71 (6H, d, J = 6.9 Hz, 2\CH₃); δ_C (CDCl₃): 142.5 (br), 128.7, 127.7, 125.8 (2\Ar-C₆), 119.0 (4-,4',-6-,6'-C), 112.0 (br, 2-,2'-3a-,3a'-,6a-,6a'-C), 58.8 (br, 2\CHCH₃), 22.2 (br, 2\CH₃); ν_{max} (ATR): 2972, 2926, 1453, 1373, 1360, 1297, 1260, 1139, 1123, 1074, 1044, 1008, 991, 915, 792, 776, 757, 703, 693, 606, 544, 520, 493cm⁻¹; m/z : (EI) 490 [M]⁺; HRMS (EI) found: [M]⁺ 490.0659, C₂₆H₂₂N₂S₄ requires: 490.0660; found C, 63.55; H, 4.37; N, 5.60%; C₂₆H₂₂N₂S₄ requires C, 63.51; H, 4.52; N, 5.71%; ²⁹³[α]_D = +48.1° (c = 0.4, CHCl₃); 9: m.p. 182-184°C; δ_H (CDCl₃): 8.38 (2H, d, J = 7.7 Hz, 2\Ar-H₁), 7.79 (2H, dd, J = 7.7, 1.9 Hz, 2\Ar-H₁), 7.68 (2H, d, J = 8.1 Hz, 2\Ar-H₁), 7.56 (2H, d, J = 6.9 Hz, 2\Ar-H₁), 7.40 (6H, m, 2\Ar-H₁), 4.45 (2H, q, J = 6.6 Hz, 2\CHCH₃), 3.57 (8H, m, 4-,4',-6-,6'-H₂), 1.46 (6H, d, J = 6.6 Hz, 2\CH₃); δ_C (CDCl₃): 139.8, 134.0, 130.8, 128.8, 127.6, 125.8, 125.5, 125.4, 124.9, 123.5 (2\Ar-C₁₀), 129.6 (3a-,3a'-,6a-,6a'-C), 117.0 (2-,2'-C), 62.0(CHCH₃), 56.0 (4-,4',-6-,6'-C), 21.9 (CH₃); ν_{max} (ATR): 2974, 2929, 2872, 1512, 1440, 1414, 1378, 1345, 1333, 1140, 1118, 1076, 1051, 983, 793, 773, 733, 701, 493cm⁻¹; m/z : (CI) 591 [M-3H]⁺ (2), 222 (100); found C, 68.69; H, 4.97; N, 4.61%; C₃₄H₃₀N₂S₄ requires C, 68.65; H, 5.08; N, 4.71%; ²⁹³[α]_D = +14.0° (c = 0.6, CHCl₃); 10: m.p. >250°C (dec.); δ_H (CDCl₃): 7.86 (2H, m, 2\Ar-H₁), 7.80 (2H, m, 2\Ar-H₁), 7.74 (2H, d, J = 8.2 Hz, 2\Ar-H₁), 7.44 (4H, m, 2\Ar-H₂), 7.36 (2H, t, J = 7.63 Hz, 2\Ar-H₁), 7.15 (2H, d, J = 7.0 Hz, 2\Ar-H₁), 6.48 (4H, s, 4-,4',-6-,6'-H), 5.95 (2H, br, 2\CHCH₃), 1.85 (6H, d, J = 6.9 Hz, 2\CH₃); δ_C (CDCl₃): 137.4, 133.8, 130.5, 130.5, 129.0, 126.7, 125.8, 125.5, 123.4, 122.4 (2\Ar-C₁₀), 119.1 (4-,4',-6-,6'-C), 111.4 (br, 2-,2'-3a-,3a'-,6a-,6a'-C), 55.8 (CHCH₃), 21.8 (CH₃); ν_{max} (ATR): 3065, 2980, 1599, 1511, 1485, 1374, 1359, 1294, 1253, 1238, 1198, 1170, 1118, 1091, 1020, 991, 199, 775, 760, 722, 648, 612, 569, 531, 505, 459cm⁻¹; m/z : (EI) 590 [M]⁺; HRMS (EI) found: [M]⁺ 590.0977, C₃₄H₂₆N₂S₄ requires: 590.0973; found C, 68.97; H, 4.33; N, 4.67%; C₃₄H₂₆N₂S₄ requires C, 69.11; H, 4.44; N, 4.74%; ²⁹³[α]_D = -239.0° (c = 0.2, THF).

14. MoK α (λ = 0.71073 Å) radiation, T = 120 K; *Crystal data* for 7: C₂₆H₂₆N₂S₄, M_r = 494.73, triclinic, a = 5.9951(12), b = 6.5877(13), c = 15.830(3) Å, α = 86.69(3), β = 83.08(3), γ = 76.01(3)°, V = 602.0(2) Å³, Z = 1, $P1$, ρ_c = 1.36 g cm⁻³, μ = 0.41 mm⁻¹, 5201 unique reffs, 4924 with $F_o > 4\sigma(F_o)$, R_{int} = 0.029, Flack parameter = 0.11(6), R_I = 0.044, wR_1 = 0.123; for 8: C₂₆H₂₂N₂S₄, M_r = 490.70, tetragonal, a = b = 7.4847(4), c = 42.565(3) Å, V = 2384.5(3) Å³, Z = 4, $P4_32_1$, ρ_c = 1.37 g cm⁻³, μ = 0.42 mm⁻¹, 2670 unique reffs, 1765 with $F_o > 4\sigma(F_o)$, R_{int} = 0.097, Flack parameter = 0.0(3), R_I = 0.089, wR_1 = 0.131; Refinement in space group $P4_32_1$, using the known absolute configuration of 8, gave a Flack parameter of 0.99(26); for 9: C₃₄H₃₀N₂S₄, M_r = 594.84, monoclinic, a = 12.705(3), b = 6.1713(12), c = 19.492(4) Å, β = 108.72(3)°, V = 1447.5(5) Å³, Z = 2, $P2_1$, ρ_c = 1.37 g cm⁻³, μ = 0.36 mm⁻¹, 6504 unique reffs, 4594 with $F_o > 4\sigma(F_o)$, R_{int} = 0.078, Flack parameter = -0.11(16), R_I = 0.080, wR_1 = 0.134; for 10: C₃₄H₂₆N₂S₄, M_r = 590.81, orthorhombic, a = 10.8652(2), b = 10.8969(2), c = 47.0032(10) Å, V = 5565.04(19) Å³, Z = 8, $C222_1$, ρ_c = 1.41 g cm⁻³, μ = 0.37 mm⁻¹, 6318 unique reffs, 5904 with $F_o > 4\sigma(F_o)$, R_{int} = 0.049, Flack parameter = 0.10(11), R_I = 0.057, wR_1 = 0.154; X-ray crystal structure were solved and refined with the SHELXS-97 and SHELXL-97 package; G.M. Sheldrick, *Acta Crystallogr.*, **2008**, *A64*, 112. Illustrations with computer packages ORTEP-3 for Windows, L.J. Farrugia, *J. App. Cryst.*, **1997**, *30*, 565. Mercury, C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields,

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