

Enhanced Electrical Conductivity in a Substitutionally Doped Spiro-bis(phenalenyl)boron Radical Molecular Solid

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S Supporting Information

ABSTRACT: We report the crystallization of a substitutionally doped organic conductor based on a host lattice composed of spiro-bis(phenalenyl)boron radicals. Co-crystallization of solutions of spiro-bis(9-oxido-phenalene)boron radical $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ mixed with selected amounts of spiro-bis(9-oxido-phenalene)beryllium $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ leads to the formation of a series of solid-state solutions of composition $[\text{PLY}(\text{O},\text{O})]_2\text{B}_{(1-x)}\text{Be}_x$. The dopant molecules $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ serve to introduce holes into the lattice of spins provided by the $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ radicals and lead to a systematic increase in the conductivity while decreasing the activation energy of the conduction process and leaving the solid-state structure relatively unperturbed. While the energies of the hole sites are expected to be high, the results are consistent with the interpretation of the electronic structure of $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ in terms of the resonating valence bond model.

Organic conductors usually rely on the interstitial doping of a neutral molecule to generate carriers in the lattice, and thus the solid-state structures of the neutral molecule and the charge-transfer salt are quite distinct. An exception to this behavior is the metal-doped fullerenes, in which the alkali metals fit within the interstitial sites of the C_{60} molecules to give conductors and superconductors with relatively unperturbed solid-state structures.^{1,2} The continuing interest in design strategies which seek to avoid the use of charge-transfer salts³ has led to important progress in single-component and neutral radical conductors and the realization of molecular metals^{4–7} and superconductors.⁸

Substitutional doping is an important industrial process, most notably in the semiconductor industry, where crystalline silicon is doped with atoms from neighboring columns of the periodic table such as boron or nitrogen to create holes or electrons in the lattice. To our knowledge, such an approach has not been successfully employed with organic molecular solids.⁹ By making use of a host lattice based on a spiro-bis(phenalenyl)boron neutral radical, $[\text{PLY}(\text{O},\text{O})]_2\text{B}$, we report the first example of a substitutionally doped organic conductor in which the carrier concentration is systematically varied by the introduction of dopant molecules into the lattice which differ only by the replacement of boron with beryllium. The spiro-bis(phenalenyl)beryllium dopant molecules $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ are also neutral, but because they possess one less valence

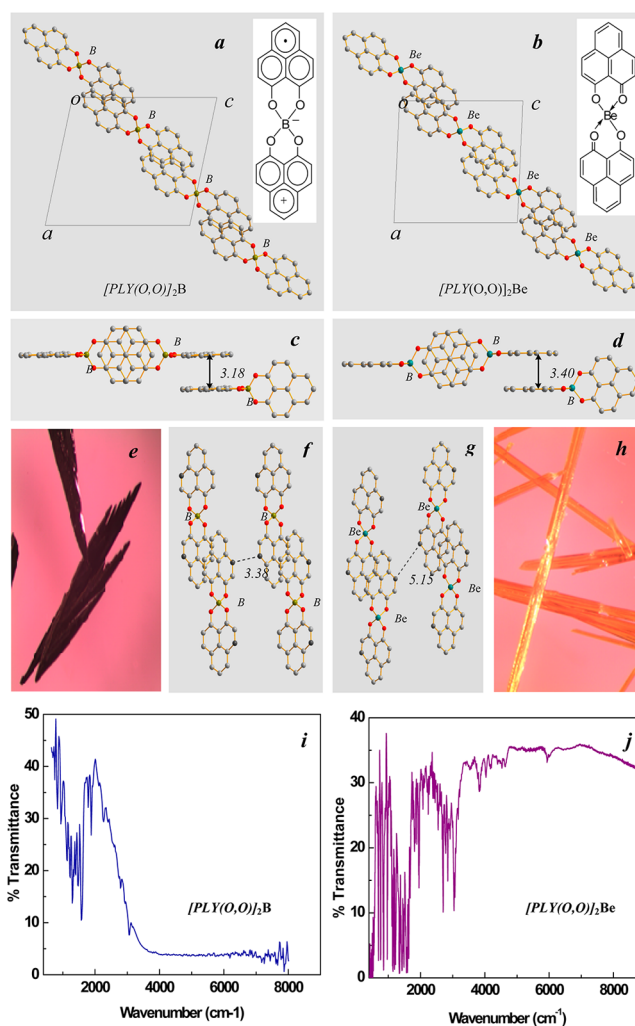


Figure 1. Single-crystal X-ray structures and transmission spectra of $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ and $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$: (a,b) 1D π -chains; (c,d) interplanar π - π separations; (e,h) pictures of crystals; (f,g) interchain contacts; (i,j) transmittance spectra of the crystals.

electron, they serve to introduce holes into the lattice in much the same sense that a boron atom can introduce a hole state close to the valence band of silicon.

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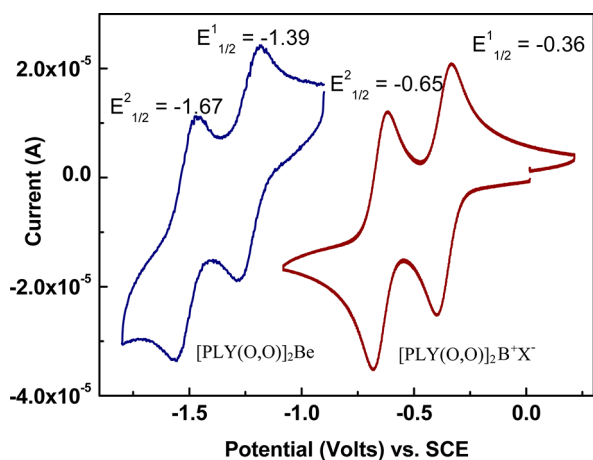


Figure 2. Electrochemical reduction potential of $[\text{PLY}(\text{O},\text{O})]_2\text{B}^+\text{X}^-$ and $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$. Cyclic voltammety of $[\text{PLY}(\text{O},\text{O})]_2\text{B}^+\text{X}^-$ ($\text{X} =$ tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, TFPB) and $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ in acetonitrile.

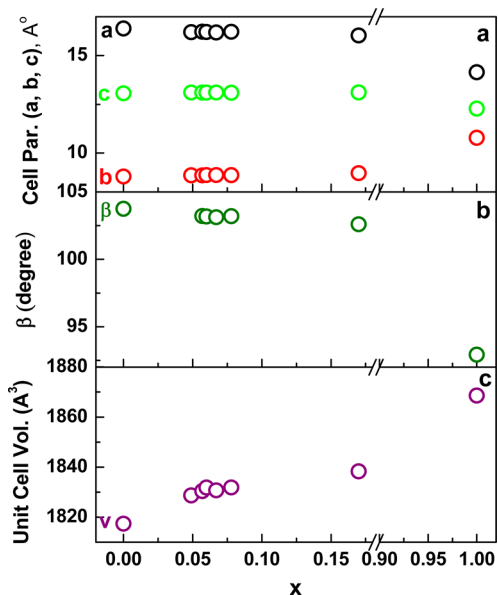


Figure 3. Plots of crystallographic parameters of $[\text{PLY}(\text{O},\text{O})]_2\text{B}_{(1-x)}\text{Be}_x$ within the $C2/c$ space group. Unit cell parameters as a function of Be concentration in $[\text{PLY}(\text{O},\text{O})]_2\text{B}_{(1-x)}\text{Be}_x$: (a) lattice parameters a , b , c (in Å); (b) lattice parameter β (degree); (c) unit cell volume, v (Å^3).

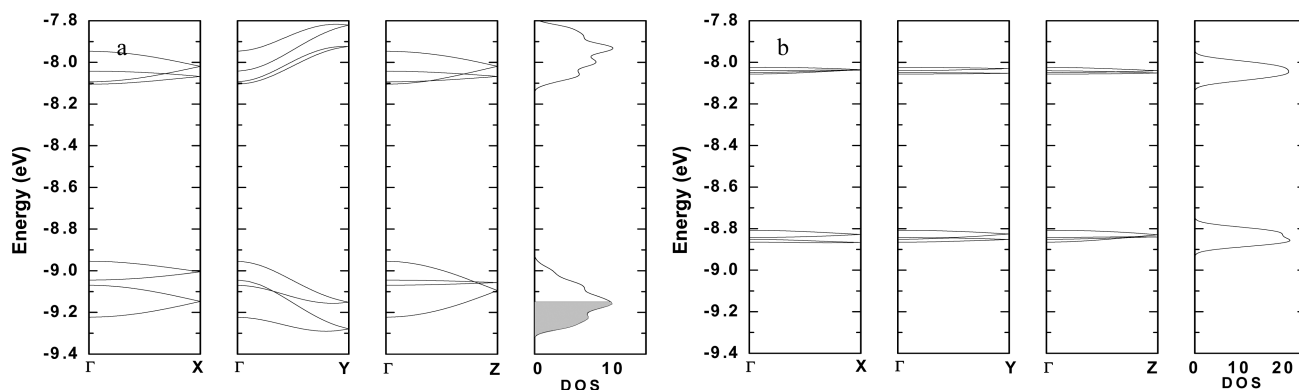
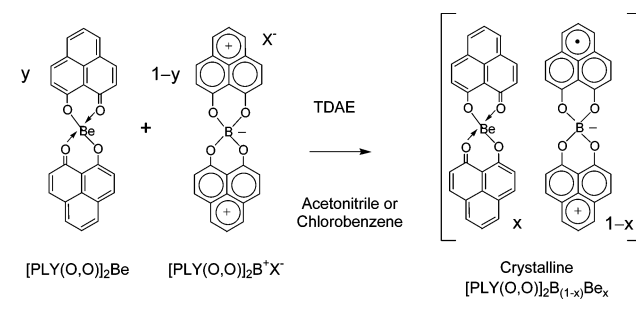


Figure 4. EHT band structure and DOS (states per eV per mol) calculated for the experimental structure of crystalline (a) $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ and (b) $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$. [$\Gamma = (0, 0, 0)$; $X = (1/2, 0, 0)$; $Y = (0, 1/2, 0)$; and $Z = (0, 0, 1/2)$], where the coordinates are given in units of the reciprocal lattice vectors. The shaded region indicates the occupied states.

Scheme 1. Synthesis of $[\text{PLY}(\text{O},\text{O})]_2\text{B}_{(1-x)}\text{Be}_x$ Crystals by Chemical Reduction



The system of choice for this study is the parent spiro-bis(9-oxidophenalenone)boron radical, $[\text{PLY}(\text{O},\text{O})]_2\text{B}$, which forms a highly symmetrical π -chain structure along the $[1\ 0\ 1]$ direction in the crystal lattice (Figure 1).¹⁰ Related compounds give room-temperature conductivities which reach $\sigma_{\text{RT}} = 0.3$ S/cm,^{10,11} and detailed electronic structure calculations have been reported.^{12,13} We have rationalized the behavior of these compounds in terms of the resonating valence bond (RVB) ground state,^{10,11} and one of the more interesting predictions for this electronic structure is an increase in the conductivity on doping away from the perfect pairing antiferromagnetic state.^{14,15} The appropriate dopant in the present connection is the analogous spiro-bis(9-oxidophenalenone)beryllium molecule, $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ (Figure 1).¹⁶

Details of the solid-state structures of the pure compounds are collected in Figure 1. Both compounds crystallize in the $C2/c$ space group ($Z = 4$), and their structures are dominated by the formation of 1D π -chains which run along the $[1\ 0\ 1]$ direction. While the molecular geometries and their solid-state structures are strongly related (Figure 1a,b), the presence of spins in the lattice of $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ leads to important distinctions in the modes of molecular packing. First, the distances between the planes of the phenalenyl (PLY) units along the π -chains are found to be 3.18 Å for $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ (Figure 1a) and 3.40 Å for $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ (Figure 1b), and second, the interactions between the π -chains are also quite distinct (Figure 1f,g). The closest approach between spin-bearing carbon atoms in neighboring chains of $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ is 3.38 Å, whereas the same pair of carbon atoms in the lattice of $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ is separated by 5.15 Å. These interactions

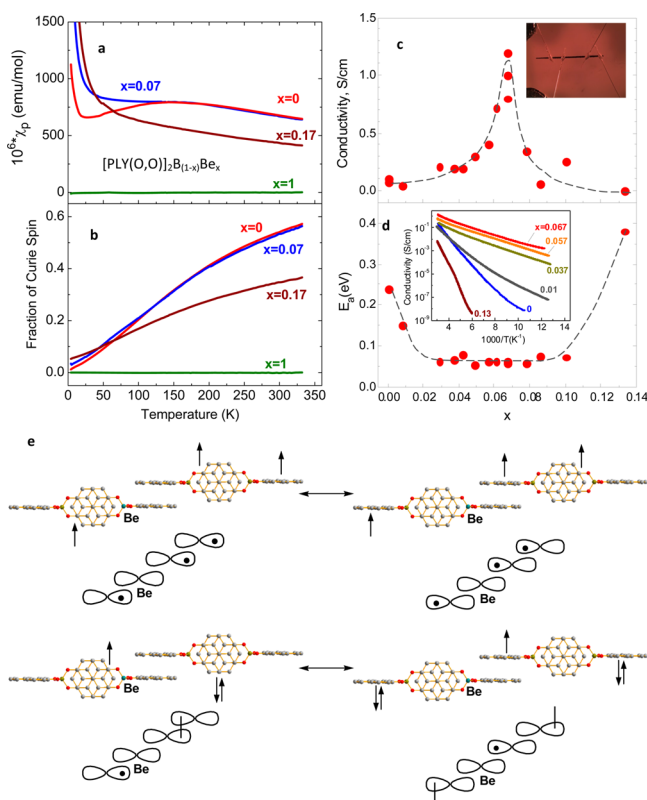


Figure 5. Electrical and magnetic properties as a function of temperature and RVB model. (a) Magnetic susceptibility of $[\text{PLY}(\text{O},\text{O})]_2\text{B}_{(1-x)}\text{Be}_x$ ($x = 0, 0.067, 0.17$, and 1). (b) Fraction of Curie spins. (c) Conductivity (S/cm) as a function of beryllium concentration (inset, picture of crystal wired for four-probe conductivity measurement). (d) Activation energy (eV) as a function of beryllium concentration (inset, single-crystal conductivity as a function of reciprocal temperature). (e) Lewis free radical resonance structures and the corresponding RVB resonance structure for $[\text{PLY}(\text{O},\text{O})]_2\text{B}_{(1-x)}\text{Be}_x$. The spiro-bis(phenalenyl) structure is represented as a figure-eight for convenience.

lead to profound changes in the unit cell parameters and are discussed in detail below.

Substitutionally doped crystals of composition $[\text{PLY}(\text{O},\text{O})]_2\text{B}_{(1-x)}\text{Be}_x$ were prepared from solutions of $[\text{PLY}(\text{O},\text{O})]_2\text{B}^+\text{X}^-$ ($\text{X} = \text{tetrakis}[3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl}]\text{borate}$, TFPB) and $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ in solvents such as acetonitrile or chlorobenzene by reduction with tetrakis(dimethylamino)ethylene (TDAE) in anaerobically prepared H-cells or by direct mixing in a glovebox. The electrochemistry of the two precursors is shown in Figure 2, and it may be seen that $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ is much more difficult to reduce than $[\text{PLY}(\text{O},\text{O})]_2\text{B}^+\text{X}^-$; thus, the crystallization process is driven by the insolubility of radical $[\text{PLY}(\text{O},\text{O})]_2\text{B}$, which apparently induces the co-crystallization of $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$.

There is both experimental and theoretical evidence to support the strong π -association of pairs of PLY units which together possess one or two spins (pancake bonding),^{17–21} and this interaction is apparently sufficient to ensure an appreciable concentration of $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ in the final structures. We were thus able to prepare a series of $[\text{PLY}(\text{O},\text{O})]_2\text{B}_{(1-x)}\text{Be}_x$ crystals of composition $0 \geq x > 0.2$, as determined by direct ICP chemical analysis of the amount of beryllium in the samples. It was reasonably straightforward to produce crystals with low levels of $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ in the lattice of

$[\text{PLY}(\text{O},\text{O})]_2\text{B}$, and starting solutions containing 10% $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ on a molar basis ($y = 0.1$, Scheme 1) lead to crystals of composition $x = 0.05$ (95% $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ and 5% $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$).

Attempts to fully control the concentration of $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ in the lattice were not successful, and even when the starting solutions consisted of 90% $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ on a molar basis ($y = 0.9$, Scheme 1), it was impossible to prepare crystalline solid solutions beyond a composition of about $x = 0.2$, due to the large packing differences in the two compounds occasioned by the presence of spins in the lattice of $[\text{PLY}(\text{O},\text{O})]_2\text{B}$. The results of X-ray crystallographic analyses of selected crystals are shown in Figure 3, and while the unit cell volumes differ by only 2.8% in crystals of $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ and $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$, the b -axis (Figure 1a) shrinks by 18.5%, and all of the unit cell parameters change by more than 5% (Figure 3).

The pronounced changes in the unit cell parameters clearly originate from the intermolecular interactions which develop in the lattice of $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ (Figure 1) and are reflected in the band structure calculations, which show strong band dispersions along the principal reciprocal space lattice vectors of crystalline $[\text{PLY}(\text{O},\text{O})]_2\text{B}$, in contrast to the narrow-band electronic structure of $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ (Figure 4). Thus, in spite of the almost identical molecular structures of $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ and $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$,²² the large differences in the unit cell parameters of the two compounds dictate a rather narrow range of stable solid-state solutions which can be experimentally realized.

The magnetic and conductivity data for crystals of $[\text{PLY}(\text{O},\text{O})]_2\text{B}$, $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$, and $[\text{PLY}(\text{O},\text{O})]_2\text{B}_{(1-x)}\text{Be}_x$ are summarized in Figure 5. It may be seen that the introduction of diamagnetic $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ into the lattice of $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ serves to decrease the magnetism in the high-temperature regime of the doped crystals $[\text{PLY}(\text{O},\text{O})]_2\text{B}_{(1-x)}\text{Be}_x$ ($x > 0$) but leads to a small increase in Curie spins at low temperatures, presumably as a result of uncoupled spins introduced by the doping process (see below). The conductivity of the doped material $\{[\text{PLY}(\text{O},\text{O})]_2\text{B}_{(1-x)}\text{Be}_x, x > 0\}$ achieves its maximum value in the vicinity of $x = 0.07$, where $\sigma_{\text{RT}} \approx 1$ S/cm, which is an order of magnitude increase over the value ($\sigma_{\text{RT}} = 0.1$ S/cm)¹⁰ reported for pure crystals of $[\text{PLY}(\text{O},\text{O})]_2\text{B}$. Likewise, the activation energy of the conductivity (Δ) falls by a factor of 5 to a value of $\Delta = 0.05$ eV for $0.03 > x > 0.1$. The room-temperature conductivity of $[\text{PLY}(\text{O},\text{O})]_2\text{B}_{0.93}\text{Be}_{0.07}$ is the highest of any neutral molecular solid composed solely of first- and second-row elements and the highest of any ambient-pressure neutral radical conductor.^{6,7}

The improvement in the conductivity parameters of the doped materials $[\text{PLY}(\text{O},\text{O})]_2\text{B}_{(1-x)}\text{Be}_x$, $x > 0$, is surprising based on the cyclic voltammetry results of the parent compounds (Figure 2), which allow an estimate of the relative energy levels of $[\text{PLY}(\text{O},\text{O})]_2\text{B}$ and $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ in the solid state.^{23,24} Based on the solution electrochemistry (Figure 2), the energy for the process $[\text{PLY}(\text{O},\text{O})]_2\text{B} + [\text{PLY}(\text{O},\text{O})]_2\text{Be} \rightarrow [\text{PLY}(\text{O},\text{O})]_2\text{B}^+ + [\text{PLY}(\text{O},\text{O})]_2\text{Be}^-$ is estimated as $\Delta E = E_{1/2}([\text{PLY}(\text{O},\text{O})]_2\text{Be}) - E_{1/2}([\text{PLY}(\text{O},\text{O})]_2\text{B}) = -1.03$ eV. Thus, based on the arguments used in the introduction, which rely on the properties of substitutionally doped semiconductors such as silicon, the beryllium molecule $[\text{PLY}(\text{O},\text{O})]_2\text{Be}$ should not provide a site in the crystal that is accessible to the conduction electrons and therefore should not be capable of contributing to the conductivity, as the states associated with

[PLY(O,O)]₂Be are expected to lie much too far above the conduction band.

However, we suggested that the properties of molecular crystals such as [PLY(O,O)]₂B^{10,11} are best explained with the RVB ground state of Pauling²⁵ and Anderson,^{14,15} and in this situation, doping away from the perfect pairing antiferromagnetic RVB state envisaged by Pauling should increase the conductivity.¹⁵ Unfortunately, the conductivity in [PLY(O,O)]₂B_(1-x)Be_x remains activated (Figure 5), but it seems that lowering the reduction potential of the dopant [PLY(O,O)]₂Be by appropriate substitution might lead to metallic alloys of substitutionally doped spiro-bis(phenalenyls) such as [PLY(O,O)]₂B_(1-x)Be_x and this encourages the pursuit of substitutional doping in organic molecular crystals. Furthermore, the conductivity attained in [PLY(O,O)]₂B_{0.93}Be_{0.07} ($\sigma_{RT} \approx 1$ S/cm) approaches quite closely the pressure-induced metallization conductivities of $\sigma_{RT} = 2\text{--}10$ S/cm reported for heteroatom-based neutral radical molecular conductors.^{6,7}

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details of the synthesis, X-ray analysis, cyclic voltammetry, near- and mid-infrared transmission spectroscopy, conductivity, magnetic susceptibility measurements, and ICP analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ Notes

The authors declare no competing financial interest.

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