

Angular (*cis*-stilbazole) geometry in octahedral dimethyldihalidoplatinum(IV) complexes: potential as metallomesogens and X-ray structure of [PtMe₂I₂(NC₅H₄CH=CHC₆H₄OC₇H₁₅)₂]

Paul Beagley, Earl J. Starr, John Bacsá, John R. Moss*, Alan T. Hutton*

Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa

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Abstract

The synthesis and characterisation of a series of octahedral dimethyldihalidoplatinum(IV) complexes of 4-alkoxy-4'-stilbazoles with the general formula [PtMe₂X₂(NC₅H₄CH=CHC₆H₄OR)₂] (X = I or Br, R = *n*-alkyl) is described. Some of the complexes show mesogenic behaviour. The structure of the complex with X = I and R = C₇H₁₅ has been determined by X-ray crystallography, revealing a *cis* coordination geometry with respect to both the methyl and the substituted 4-alkoxy-4'-stilbazole (*n*-OST) ligands. © 2002 Elsevier Science B.V. All rights reserved.

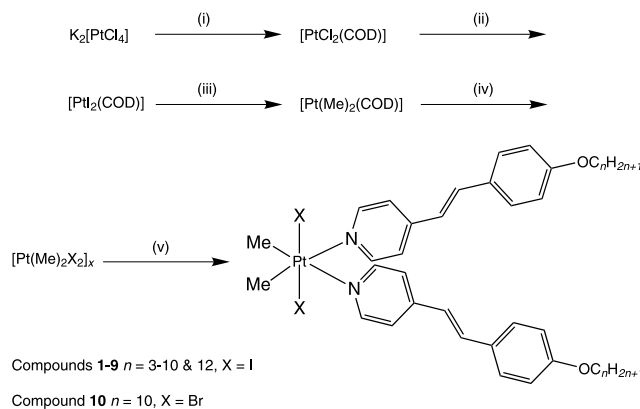
Keywords: Platinum(IV); Metallomesogen; 4-Alkoxy-4'-stilbazole; Crystal structure

1. Introduction

Numerous examples of platinum-containing mesogens have been reported [1]. In all of these complexes, there is a square-planar arrangement of ligands about the metal atom. These complexes generally contain two pro-mesogenic ligands that may, but need not, be the same, and are exclusively *trans*-disposed about the platinum, giving an anisotropic, rod-shaped molecule.

The reactions of the dimethylplatinum(IV) complexes [PtMe₂X₂]_x with a variety of neutral or uninegative ligands have been extensively studied [2], showing that the bridges formed by the halogen atoms in the oligomer are broken by the incoming ligands L to give the monomeric octahedral complexes [PtMe₂X₂L₂], in which the ligands L display a *cis* geometry about the metal atom. Thus, the aim of this work was to synthesise octahedral complexes of the type [PtMe₂X₂(*n*-OST)₂] (*n*-OST = 4-alkoxy-4'-stilbazole, Scheme 1) that

might be expected to show *cis* geometry with respect to the 4-alkoxy-4'-stilbazole (*n*-OST) ligands. Since 4-alkoxy-4'-stilbazole ligands are well-known in metallomesogen chemistry [3], it was envisaged that they might confer liquid-crystalline properties upon these octahedral and V-shaped complexes.



Scheme 1. Synthesis of complexes 1–10. Reagents and conditions: (i) 1,5-cyclooctadiene, *n*-PrOH, H₂O; (ii) NaI, acetone; (iii) MeLi, Et₂O; (iv) X₂, CH₂Cl₂; and (v) 4-alkoxy-4'-stilbazole, CH₂Cl₂.

* Corresponding authors. Tel.: +27-21-6502535; fax: +27-21-6897499.

E-mail addresses: jrm@science.uct.ac.za (J.R. Moss), athutton@science.uct.ac.za (A.T. Hutton).

Table 1
Yields and microanalyses for complexes 1–10

Compound no.	<i>n</i>	Yield ^a (%)	Microanalysis ^b		
			%C	%H	%N
1	3	75	42.6 (42.65)	4.15 (4.2)	2.6 (2.9)
2	4	66	44.3 (43.9)	4.5 (4.5)	2.5 (2.8)
3	5	68	45.0 (45.0)	4.7 (4.8)	2.5 (2.75)
4	6	58	46.1 (46.1)	4.9 (5.0)	2.7 (2.7)
5	7	65	46.8 (47.2)	5.2 (5.3)	2.3 (2.6)
6	8	79	48.5 (48.15)	5.6 (5.5)	2.6 (2.55)
7	9	70	49.0 (49.1)	5.7 (5.5)	2.25 (2.5)
8	10	80	49.95 (49.9)	6.0 (5.9)	2.3 (2.4)
9	12	72	51.95 (51.6)	6.4 (6.3)	2.2 (2.3)
10	10	62	54.3 (54.4)	6.5 (6.5)	2.3 (2.6)

^a Based on the theoretical yield relative to $[\text{Pt}(\text{CH}_3)_2\text{X}_2]_x$.

^b Found (calculated).

2. Experimental

2.1. General

The syntheses were performed using standard Schlenk techniques; $[\text{PtMe}_2\text{I}_2]_x$ [4] and the 4-alkoxy-4'-stilbazole ligands [5] were prepared according to literature methods. Dichloromethane was distilled from CaH_2 . ^1H and ^{13}C NMR spectra were recorded at room temperature on a Varian EM 400 MHz spectrometer. ^1H NMR spectra were referenced internally using the residual protons in the deuterated solvent (CDCl_3 ; δ 7.27) and are reported relative to tetramethylsilane (δ 0.00). ^{13}C NMR spectra were referenced internally to the solvent resonance (CDCl_3 ; δ 77.0) and are reported relative to tetramethylsilane (δ 0.0). Infrared spectra were recorded as Nujol mulls on a Perkin–Elmer Paragon 1000 FT-IR spectrometer. Melting points were performed on a Kofler hot-stage microscope (Reichert–Thermovar). Optical characterisation of the mesophases was performed by viewing the sample through crossed polarisers attached to the hot-stage microscope. Elemental analyses were performed using a Carlo Erba EA1108 elemental analyser in the microanalytical laboratory of the University of Cape Town.

2.2. Preparation of complex 5

This is a representative synthesis for complexes of the type $[\text{PtMe}_2\text{X}_2(n\text{-OST})_2]$. The ligand ($n\text{-OST}$, $n = 7$) (78 mg, 0.250 mmol) was dissolved in CH_2Cl_2 (1 cm^3) and added to a suspension of $[\text{PtMe}_2\text{I}_2]_x$ (60 mg, 0.125 mmol) in CH_2Cl_2 (4 cm^3). After stirring for 18 h, the resulting mixture was centrifuged and the orange supernatant decanted, leaving a thin layer of unreacted $[\text{PtMe}_2\text{I}_2]_x$. The solvent volume was reduced by about half and MeOH (2 cm^3) was added to give **5** as an orange solid that was isolated by filtration and dried in

vacuo (113 mg, 65%); ^1H NMR (400 MHz): 8.94 (4H, AA'XX', $^3J_{\text{PtH}} = 20$ Hz, $^3J_{\text{HH}} = 7$ Hz, py-H_a), 7.48 (4H, AA'XX', $^3J_{\text{HH}} = 9$ Hz, Ar-H_g), 7.34 (4H, AA'XX', $^3J_{\text{HH}} = 7$ Hz, py-H_b), 7.33 (2H, AB, $^3J_{\text{HH}} = 16$ Hz, H_e), 6.91 (4H, AA'XX', $^3J_{\text{HH}} = 9$ Hz, Ar-H_h), 6.86 (2H, AB, $^3J_{\text{HH}} = 16$ Hz, H_d), 4.00 (4H, t, $^3J_{\text{HH}} = 7$ Hz, H_j), 2.51 (6H, s, $^2J_{\text{PtH}} = 72$ Hz, Pt-CH₃), 1.83 (4H, m, H_k), 1.42 (4H, m, H_l), 1.31 (6H, m, H_m), 0.89 (6H, t, $^3J_{\text{HH}} = 7$ Hz, H_n); ^{13}C NMR (100 MHz): 160.4 (C_i), 153.3 (C_a), 147.1 (C_c), 135.6 (C_e), 128.8 (C_g), 128.0 (C_f), 121.9 (C_d), 121.8 (C_b), 114.9 (C_h), 68.2 (C_j), 31.8–22.6 (C_{k,l,m}), 14.1 C_n, –18.6 ($^1J_{\text{PtC}} = 502$ Hz, Pt-CH₃) (see Fig. 1).

Complexes 1–10 were prepared in an analogous manner and the ^1H and ^{13}C NMR data are available from the authors. Complexes 1–5 ($n = 3–7$) were crystallised from CH_2Cl_2 –MeOH and obtained as orange crystals, while complexes 6–10 ($n = 8–10$ and 12) separated as viscous orange–brown oils that solidified upon standing for two days at -15 °C. The IR spectra (Nujol mulls) of all the complexes showed a single, weak $\nu(\text{Pt}-\text{C})$ absorption in the range 546–552 cm^{-1} . Table 1 gives the yields and elemental analyses for the complexes 1–10.

2.3. X-ray crystallography

Crystals of complex 5 that were suitable for X-ray diffraction study were obtained by slow diffusion of

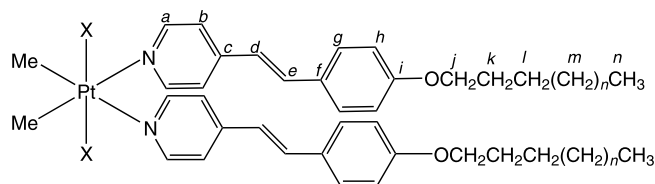


Fig. 1. Labelling scheme for the NMR assignments of complexes 1–10.

Table 2
Crystal data and structure refinement parameters for **5**

Empirical formula	C ₄₂ H ₅₆ I ₂ N ₂ O ₂ Pt
Formula weight	1069.78
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	8.757(1)
<i>b</i> (Å)	27.838(2)
<i>c</i> (Å)	17.757(1)
β (°)	91.623(7)
<i>V</i> (Å ³)	4327.0(6)
<i>Z</i>	4
<i>D</i> _{calc} (Mg m ⁻³)	1.642
Absorption coefficient (mm ⁻¹)	4.704
<i>F</i> (000)	2088
Crystal size (mm)	0.37 × 0.35 × 0.33
Theta range for data collection (°)	2.29–28.37
Index ranges	–10 ≤ <i>h</i> ≤ 11, –36 ≤ <i>k</i> ≤ 36, –23 ≤ <i>l</i> ≤ 23
Reflections collected	22 494
Independent reflections	9606 [<i>R</i> _{int} = 0.0368]
Completeness to theta = 28.37° (%)	88.8
Max./min. transmission	0.3059, 0.2750
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	9606/1/442
Goodness-of-fit on <i>F</i> ²	1.019
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0448, <i>wR</i> ₂ = 0.1003
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0836, <i>wR</i> ₂ = 0.1160
Extinction coefficient	0.00027(9)
Largest difference peak and hole (e Å ⁻³)	1.253 and –0.741

Table 3
Transition temperatures (°C) of complexes **1–10** as observed by thermal microscopy during the first heating run

Complex no.	<i>n</i>	<i>T</i> ₁ ^a	<i>T</i> ₂	<i>T</i> ₃ ^b
1	3	159–164		
2	4	148–157		
3	5	132–135		
4	6	112–116		
5	7	124–128		
6	8	70	145	248
7	9	75	147	240 ^c
8	10	85	151	261
9	12	86	152	254 ^c
10	10	84	165	176 ^c

^a *T*₁, melting point.

^b *T*₃, clearing point.

^c With decomposition.

MeOH into a CH₂Cl₂ solution of complex **5**. X-ray diffraction data was collected at room temperature using a Nonius Kappa CCD with 1.5 kW graphite-monochromated Mo radiation. Crystal data are given in Table 2. The strategy for the data collection was

evaluated using COLLECT [6]. Several sets of data were collected with both 360° phi and omega scans to collect the cusp data. These data were integrated using DENZO-SMN [7]. Unit cell dimensions were refined on all data. The program SCALEPACK [7] was used for scaling and treating the data for absorption. The space group *P*2₁/*c* was chosen on the basis of systematic absences in the diffraction pattern. The structure was solved and refined using SHELX97 [8]. There was some difficulty in locating the position of atoms C(22) and C(42). These atoms were placed after careful inspection of difference electron maps. The distance from the adjacent atoms C(21) or C(41) was constrained during the refinement. The thermal parameters of the terminal carbons were quite large, since these atoms do not pack together efficiently in the crystal. Hydrogen atoms were placed in positions that were chemically reasonable and refined as riding atoms. Molecular graphics were obtained with the program PLATON [9].

3. Results and discussion

A series of octahedral Pt^{IV} complexes has been synthesised in good yield (58–80%) by reaction of [PtMe₂X₂]_{*x*} (X = I or Br) with the mesogenic 4-alkoxy-4'-stilbazole (*n*-OST) ligand. The reactions were performed in CH₂Cl₂, which allowed removal of unreacted [PtMe₂X₂]_{*x*} by centrifugation. The products could then be isolated as air-stable, orange crystals or oils (that solidified at –15 °C) after the addition of MeOH.

3.1. Spectroscopic and thermal properties

Spectroscopic data indicated the *cis* geometry shown in Scheme 1. The ²*J*_{PtH} = 72 Hz (lit. [2] 72 Hz for [PtMe₂I₂(py)₂], py = pyridine) coupling in the ¹H NMR spectra and the ¹*J*_{PtC} = 502 Hz (lit. [10] 512 Hz [PtMe₂Br₂(py)₂]) coupling in the ¹³C NMR spectra for the Pt–Me resonances were consistent with literature values for analogous pyridine complexes. The 20 Hz ³*J*(Pt–N–CH) coupling demonstrates that the 4-alkoxy-4'-stilbazole ligand is coordinated to the Pt^{IV} centre; however, no platinum satellites for the analogous pyridine complexes ([PtMe₂X₂(py)₂], X = Br or I) have been reported [2]. Finally, the *cis* geometry of complex **5** was confirmed by X-ray crystallography (see Section 3.2).

The thermal behaviour of complexes **1–10** was studied by polarised optical microscopy. The transition temperatures are given in Table 3. The shorter- and medium-chain homologues **1–5** melted sharply from crystalline solids to isotropic liquids and displayed a general decrease in melting temperature as the chain length of the terminal alkoxy chains was increased. The longer-chain homologues **6–9** all showed similar behaviour which may be ascribed to the formation of one

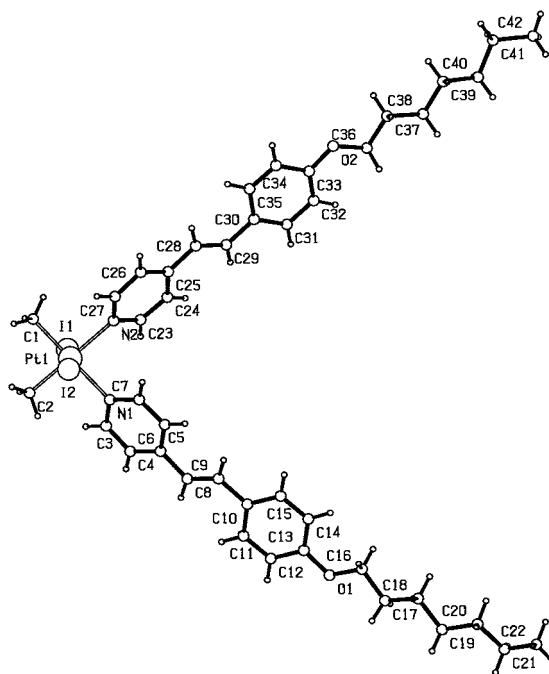


Fig. 2. Molecular structure of $[\text{PtMe}_2\text{I}_2(\text{NC}_5\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{O}-\text{C}_7\text{H}_{15})_2]$ (**5**).

Table 4
Selected bond lengths (Å) for compound **5**

Bond lengths	
Pt(1)–C(2)	2.064(6)
Pt(1)–C(1)	2.081(6)
Pt(1)–N(1)	2.194(5)
Pt(1)–N(2)	2.212(5)
Pt(1)–I(1)	2.6353(5)
Pt(1)–I(2)	2.6372(5)

Table 5
Selected bond angles (°) for compound **5**

Bond angles	
C(2)–Pt(1)–C(1)	87.2(3)
C(2)–Pt(1)–N(1)	92.9(2)
C(1)–Pt(1)–N(1)	179.8(3)
C(2)–Pt(1)–N(2)	178.8(2)
C(1)–Pt(1)–N(2)	91.6(2)
N(1)–Pt(1)–N(2)	88.3(2)
C(2)–Pt(1)–I(1)	88.7(2)
C(1)–Pt(1)–I(1)	88.3(2)
N(1)–Pt(1)–I(1)	91.56(12)
N(2)–Pt(1)–I(1)	90.94(11)
C(2)–Pt(1)–I(2)	87.6(2)
C(1)–Pt(1)–I(2)	90.3(2)
N(1)–Pt(1)–I(2)	89.9(2)
N(2)–Pt(1)–I(2)	92.8(2)
I(1)–Pt(1)–I(2)	176.1(2)

or more liquid-crystal phases. Initial melting at around 80 °C gave rise to small anisotropic platelets within a pseudo-isotropic phase. This phase persisted as the temperature was increased further until instantaneously transforming to a viscous anisotropic mesophase at around 150 °C. Further heating of the sample resulted in the gradual development of a highly coloured and viscous phase,¹ and in some cases *schlieren* textures were observed. Application of light pressure to the slide coverslip emphasised the *schlieren* texture. Close to their respective clearing points (around 250 °C), the mesophases became more fluid and isotropic regions gradually formed; however, at this temperature decomposition started to occur. The dibromido complex **10** showed similar mesogenic behaviour but it was less stable and decomposed at 176 °C.

Samples that were heated to about 170 °C (i.e. into the mesophase) and then cooled to room temperature were shown to be spectroscopically (¹H NMR) identical to the starting material. This demonstrated that the *cis* 4-alkoxy-4'-stilbazole arrangement around the octahedral platinum centre was retained in the liquid-crystalline phase. Definitive identification of these mesophases must await further characterisation. In this communication we merely indicate the potential of these metal complexes as mesogens, having developed their synthesis and unambiguously established their composition, structures and spectroscopic properties.

3.2. Molecular and crystal structure of **5**

The molecular structure of **5** is shown in Fig. 2. Bond distances and angles around the metal centre are shown in Tables 4 and 5, respectively. The most striking feature of this molecule is its V-shape. This shape is a consequence of the coordination geometry around Pt^{IV} with the two 4-alkoxy-4'-stilbazole ligands *cis* to each other. The bond angles involving Pt^{IV} are close to the octahedral values. The bond angles I–Pt–N [91.5(1)° and 90.9(1)°] are slightly larger than the N–Pt–N angle [88.3(1)°] since iodine has a larger van der Waals radius than nitrogen. The 4-alkoxy-4'-stilbazole ligands have similar geometries and show no unusual features. In both ligands, the two aromatic rings are twisted slightly relative to each other. The dihedral angles between the least-squares planes of the 4-pyridyl and the 4'-alkoxy-stilbene rings is 18.6(4)° in the first ligand and 21.5(4)° in the second ligand. The intramolecular angle C(41)⋯Pt⋯C(21) (71°) defines the angle between the ends of the two alkyl chains² and is smaller than the

¹ A photograph of complex **9** viewed through crossed polarisers at 175 °C is available from the authors.

² C(22) and C(42) could not be accurately positioned.

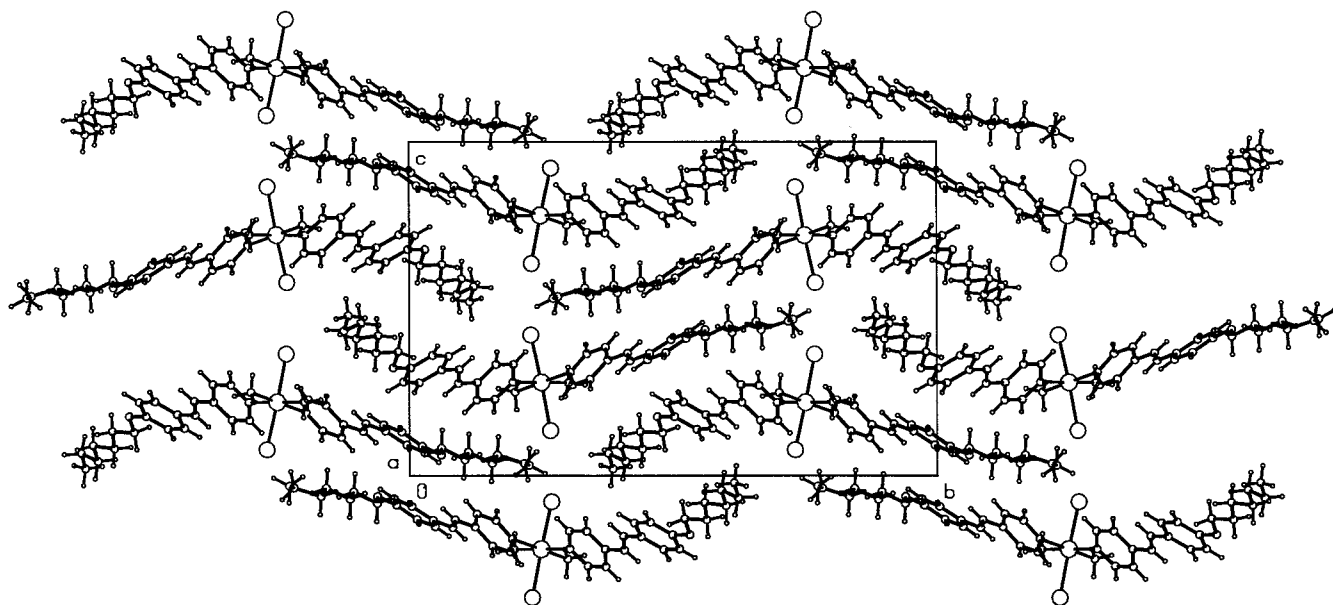


Fig. 3. Packing diagram for complex **5** viewed along the *a*-axis.

bond angle N–Pt–N [88.3(1)°]. This indicates that the 4-alkoxy-4'-stilbazole ligands curve towards each other.

The molecular packing, viewed along the *a*-axis, is shown in Fig. 3. The crystal consists of wave-like layers running parallel to the *b*-axis, creating an interdigitated herring-bone alignment of the angular molecules. There is a pair-wise association of molecules with head-to-tail and tail-to-head packing, if the Pt atom is considered to be the head. This arrangement allows the long alkyl chains of neighbouring molecules to associate with each other.

4. Conclusions

A series of Pt^{IV}-bis(4-alkoxy-4'-stilbazole) complexes has been prepared and characterised. The X-ray structure determination for complex **5** shows an octahedral arrangement of ligands around the Pt^{IV} centre. This also confirmed that the two methyl groups and the two 4-alkoxy-4'-stilbazole ligands occupy mutually *cis* positions and the iodide ligands are *trans* to one another (see Fig. 2). With the 4-alkoxy-4'-stilbazole ligands in *cis* positions, the molecule has an overall V-shape. In spite of this, complexes **6–10** showed mesogenic behaviour (see Table 3). These results are contrary to the expectation that a *trans* configuration of the extended chains, giving rise to an overall linear shape, be a prerequisite for calamitic-type thermotropic liquid-crystal behaviour. However, angular organic mesogens have been shown [11] to exhibit biaxial smectic phases with the molecules packed into herring-bone layers. The presently observed interdigitated alignment of angular complexes is thus not unreasonable.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 16595 for compound **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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