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Research Article

**Investigation of adduct formation constants of  
nickel(II)diphenylcarbazonate with nitrogen bases by  
spectrophotometry**

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**ABSTRACT**

Job's continuous variation method was employed to study the adduct formation constants of selected nitrogen bases with nickel(II)diphenylcarbazonate at  $25 \pm 0.1^\circ\text{C}$  in chloroform solution. In case of bidentate bases Job's plot displayed a maximum at a mole fraction  $X_{\text{Ni(DPC)}_2} = 0.5$ , which indicates the formation of 1:1 adducts with  $X_{\text{Ni(DPC)}_2}$ . Where as in case of monodentate bases Job's plot displayed a maximum at a mole fraction  $X_{\text{Ni(DPC)}_2} = 0.66$  indicating the formation of 1:2 adducts with  $X_{\text{Ni(DPC)}_2}$ . Variation in their stabilities of these adducts with the bases are attributed to changes in their donor power. Stability of adducts are discussed in terms of steric hindrance, basicity and ring structure. Further it is found that the formation constant values of nickel(II)diphenyl carbazonate are higher than those of nickel(II)diphenylthiocarbazonate. This was attributed to the weak Ni-N bond in nickel(II)diphenylcarbazonate.

**Keywords:** Adduct, spectrophotometer, nickel(II)diphenylcarbazonate, nitrogen bases and steric factor.

**INTRODUCTION**

Nickel plays important role in the biology of some microorganisms and plants.<sup>1-3</sup> Diphenyl carbazone is a oxygen analogue of dithizone, it is widely used in detection of several heavy metals such as Hg, Cd, Mo, Cr, Cu<sup>4-6</sup>. Ni(DPC)<sub>2</sub> is paramagnetic in nature, which is in contrast with the magnetic property of nickel(II)diphenylthiocarbazonate<sup>7</sup>. In continuation of our earlier work<sup>8</sup> on the behavior of nitrogen bases with nickel metal chelate, we have further investigated the interaction of some nitrogen bases like 2,2'-bipyridyl, 1,10-phenanthroline, ethylenediamine, aniline, substituted anilines, pyridine, substituted pyridines and other monodentate nitrogen bases with nickel(II)diphenylcarbazonate in chloroform at room temperature spectrophotometrically by using Job's continuous variation method. Much work has done on the evaluation of factors such as ligand basicity, solvent, steric effects and metal chelate acidity in the study of adducts formation from metal chelates<sup>9-16</sup>. In this report we gave some results of study of relative

importance of steric hindrance of substituted aniline, substituted pyridines and other monodentate and bidentate nitrogen bases with Ni(DPC)<sub>2</sub>.

**MATERIALS AND METHODS**

**Apparatus:** Bausch and Lomb Spectronic 2000 spectrophotometer was used to determine the composition of the complex at  $25 \pm 0.1^\circ\text{C}$ .

**Reagents:** Commercial sample of diphenylcarbazone (Robert Johnson) was purified by the method reported elsewhere<sup>17</sup> and purity was checked against the reported melting point viz.,  $127^\circ\text{C}$ . Aniline, 2-Me aniline, 3-Me aniline (B.D.H), 2,3-Dimethyl aniline, 2,4-Dimethyl aniline, 2,6-Dimethyl aniline (Merck), pyridine (Fisher), 2,4-lutidine (dimethyl analogue of pyridine), morpholine, piperidine (Merck), quinoline (B.D.H), 2-picoline, 3-picoline, 4-picoline, 2,6-lutidine (dimethyl analogue of pyridine), 2,4,6-collidine (trimethyl analogue of pyridine), ethylenediamine(B.D.H) were dried over potassium

hydroxide and distilled. The constant boiling fraction was collected and used. 4-Methyl aniline, 2,5-dimethyl aniline, 3,4-dimethyl aniline, 2,2'-bipyridyl, 1,10-phenanthroline (B.D.H) and nickel chloride hexahydrate (Merck) were used without purification.

#### Preparation of Metal Chelate:

The nickel(II)diphenylcarbazone was prepared by dissolving 1g of nickel chloride hexahydrate in 50ml of acetate buffer of pH 6, resulting solution was heated to 60°C and this hot solution was mixed with alcoholic solution of diphenylcarbazone. The total amount of reagent added was slightly more than that of required for 1:2 stoichiometry. The precipitate obtained was digested on low heat for two hour and filtered under suction, washed several times with water and finally twice with alcohol to remove unreacted metal and ligand residues. The complex obtained was dried in *vacuum* over phosphorus pentoxide at room temperature. The complex was analyzed for the metal content. The nickel content of the complex was found to be 10.89% by phenanthroline-dithizone method<sup>18</sup> and it was found to be in good agreement with calculated value (10.94%).

#### Determination of Adduct Formation Constants:

Adduct formation constants,  $K_f$  of nickel(II)diphenylcarbazone  $[\text{Ni}(\text{DPC})_2]$  with nitrogen bases have been determined by Job's method of continuous variation to find the composition of complex formed, 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10ml of  $5.9 \times 10^{-5} \text{M}$   $\text{Ni}(\text{DPC})_2$  was pipetted in to 25ml volumetric flask were mixed with 10, 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0, 1.0, 0 ml  $5.9 \times 10^{-5} \text{M}$  nitrogen base was added keeping both the number of moles of  $\text{Ni}(\text{DPC})_2$  and bidentate nitrogen base, constant but varying either mole fractions of  $\text{Ni}(\text{DPC})_2$  or ligand (where as in case of most of the monodentate bases  $5.9 \times 10^{-2} \text{M}$   $\text{Ni}(\text{DPC})_2$  and  $5.9 \times 10^{-2} \text{M}$  nitrogen bases are used).  $\lambda_{\text{max}}$  was determined using one of the composition at 400-700nm. The absorbance value at 480nm and 530nm are found to be suitable for study of formation of the  $\text{Ni}(\text{DPC})_2$  adducts, because the difference in the absorbance between  $\text{Ni}(\text{DPC})_2$  and adduct being the largest at these wavelength (Fig 1). The absorption for all the compositions was recorded at a constant wavelength

( $\lambda_{\text{max}}$ , 530nm)<sup>19</sup>. The data of absorption and percentage composition of  $\text{Ni}(\text{DPC})_2$  and ligand solution at the constant temperature ( $25 \pm 0.1^\circ \text{C}$ ) can be used and curves were constructed. A typical plot is shown in Fig 2.

#### Calculations:

The ratio of metal chelate to base was determined by constructing graph of absorbance versus mole fraction of metal chelate (Fig 2). In this work formation constants value of the adducts ( $K_f$ ) were calculated by using the following equation,<sup>20</sup>

$$K_f = \frac{[A_2/A_1]}{[1 - \frac{A_2}{A_1}] \times [C_L - C_M \times \frac{A_2}{A_1}]}$$

Where,  $K_f$  : adduct formation constant

$A_1$  : absorbance at break point

$A_2$  : actual absorbance

$C_M$  : concentration of  $[\text{Ni}(\text{DPC})_2]$

$C_L$  : concentration of base (ligand)

#### RESULTS AND DISCUSSION

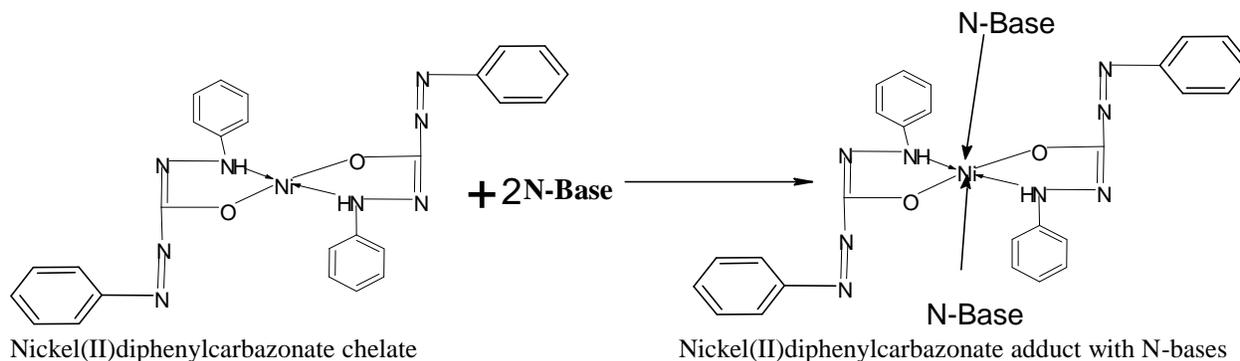
The reaction of heterocyclic bases with chelate nickel(II)diphenylcarbazone in non-aqueous solutions produces 1:2 adducts<sup>7</sup>, their stoichiometry being shown by a well defined isosbestic point and equilibrium constants of the form:

$$K = \frac{[\text{adduct}]}{[\text{diphenyl carbzionate}] \times [\text{base}]}$$

Which are highly consistent over a wide range of composition. The identity of the absorption spectra of the simple chelates in solution in pure pyridine with the extrapolated spectra of 1:2 adducts shows that two molecules of pyridine are added to the complexes under these experimental conditions.

The main purpose of our research work was to evaluate quantitatively any steric effects in the formation of adducts between  $\text{Ni}(\text{DPC})_2$  and nitrogen bases in a solvent such as chloroform.  $\text{Ni}(\text{DPC})_2$  described in previous publications<sup>21,22</sup> is paramagnetic and has been attributed tetrahedral structure with  $sp^3$  hybridization. It gives red coloured solution in solvents like  $\text{CHCl}_3$  and  $\text{CCl}_4$  etc, while the solutions in pyridine, substituted pyridine, aniline and substituted anilines are pink in colour.

This may probably due to the formation of the  $\text{Ni}(\text{DPC})_2$  and nitrogen base adducts of the following type:



The spectrum for  $\text{Ni}(\text{DPC})_2$  exhibit a  $\lambda_{\text{max}}$  at 480nm and 560nm. The spectrum of  $\text{Ni}(\text{DPC})_2$  undergoes profound change upon the addition of nitrogen bases, collapsing to a single absorption band in the visible range between 530-540 nm. The change in the spectra of  $\text{Ni}(\text{DPC})_2$  on the addition of nitrogen bases could be used to determine the equilibrium constant of the adducts<sup>7</sup>.

The absorption spectra were measured in the visible region around 400-800nm using chloroform as a reference at a concentration of  $10^{-5}\text{M}$  for bidentate bases and  $10^{-2}\text{M}$  for monodentate bases. A typical spectra for absorbance measurements gave wavelength of maximum absorbance for  $\text{Ni}(\text{DPC})_2$  complex with nitrogen bases which was found to be between 530-540nm as it is evident by graph plotted between different wavelength and absorbance (Fig 1).

The adduct formation constants of the  $\text{Ni}(\text{DPC})_2$  with nitrogen bases at  $25 \pm 0.1^\circ\text{C}$  are listed in Table 1. Column III gives the values of  $\text{pK}_a$  of N-bases that were selected for this investigation, Column IV gives the values of formation constants in  $\text{CHCl}_3$ .

The stabilities of  $\text{Ni}(\text{II})$  adducts were found to increase in the following order of bases:

2-Me aniline < 2,3-dimethyl aniline, 2,6-dimethyl aniline < 2,4-dimethyl aniline < DMSO < 2,5-dimethyl aniline < 3-Me aniline, 4-Me aniline < 3,4-dimethyl aniline < 2,6-lutidine < 2-picoline < 2,4,6-collidine < 2,4-lutidine < morpholine < quinoline < piperidine < 3-picoline < 4-picoline < pyridine < 2,2'-bipyridyl < ethylenediamine < 1,10-phenanthroline.

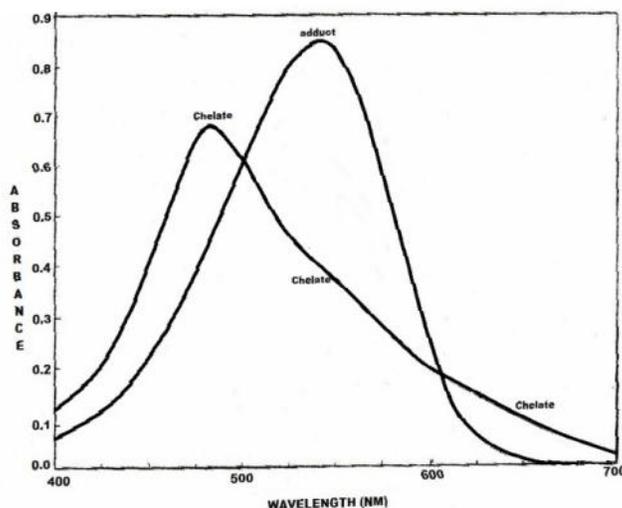
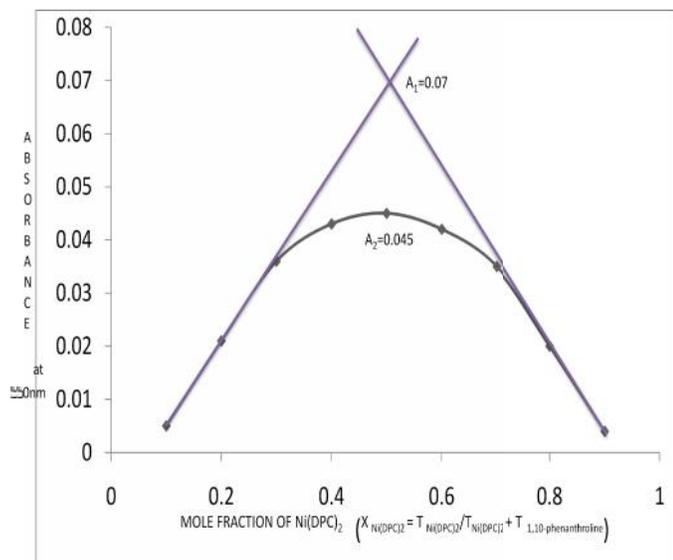
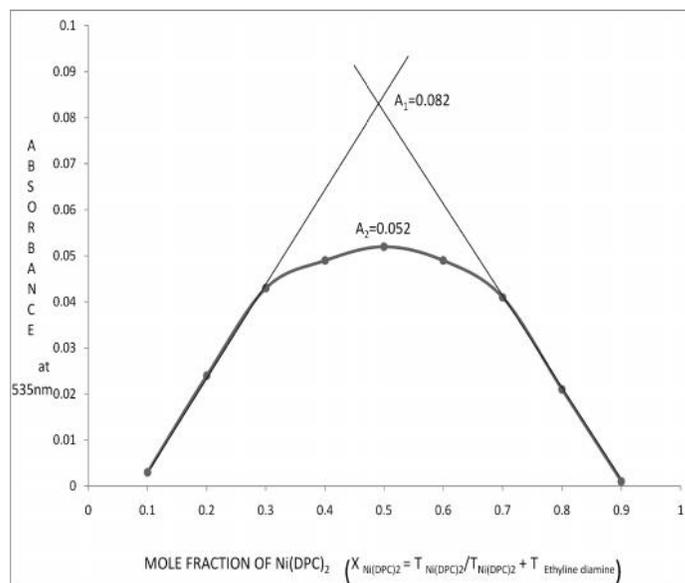


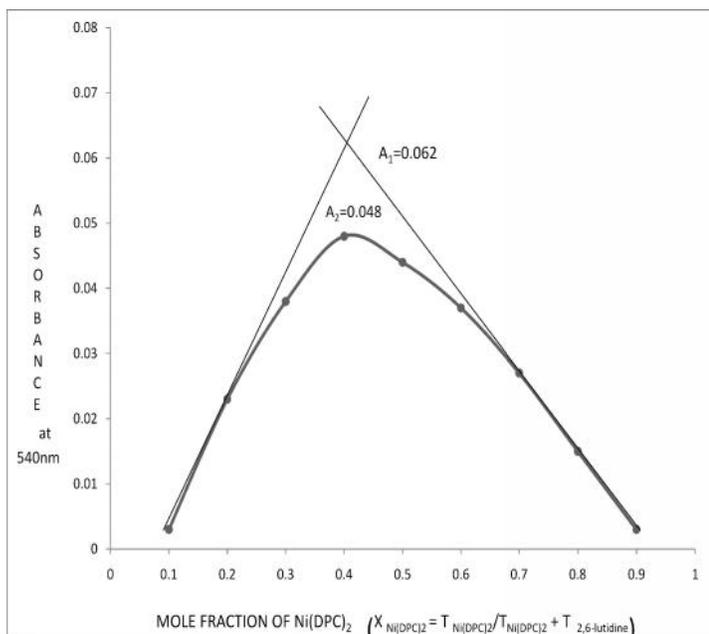
Figure 1  
Plot of absorption spectra of  $\text{Ni}(\text{DPC})_2$  and 2,4-lutidine at  $25 \pm 0.1^\circ\text{C}$  in chloroform



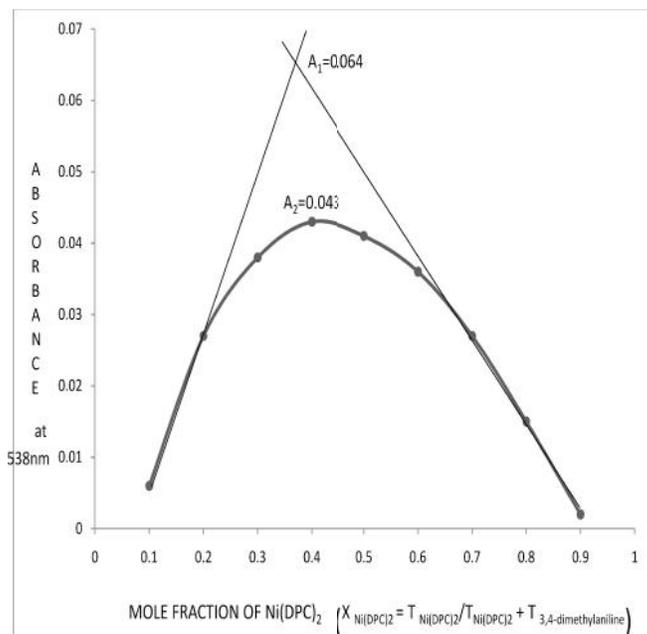
(a) Job's plot for Ni(DPC)<sub>2</sub> (5.9X10<sup>-5</sup>M) and 1,10-phenanthroline(5.9X10<sup>-5</sup>M) at 25±0.1<sup>o</sup>C in chloroform



(b) Job's plot for Ni(DPC)<sub>2</sub> (5.9X10<sup>-5</sup>M) and ethylenediamine (5.9X10<sup>-5</sup>M) at 25±0.1<sup>o</sup>C in chloroform



(c) Job's plot for Ni(dz)<sub>2</sub> (5.9X10<sup>-2</sup>M) and 2,6-lutidine (5.9X10<sup>-2</sup>M) at 25±0.1<sup>o</sup>C in chloroform



(d) Job's plot for Ni(DPC)<sub>2</sub> (5.9X10<sup>-2</sup>M) and 3,4- dimethyl aniline (5.9X10<sup>-2</sup>M) at 25±0.1<sup>o</sup>C in chloroform

**Figure 2**  
Job's curves of equimolar solutions of Ni(DPC)<sub>2</sub> – nitrogen bases at 25±0.1<sup>o</sup>C in chloroform

Table 1  
Adduct formation constants of nickel(II)diphenylcarbazonates

Sl.No.	Name of the Base	pka	logK <sub>f</sub>
1	Aniline	4.63 <sup>27</sup>	1.93
2	2Me-aniline	4.44 <sup>27</sup>	1.49
3	3Me-aniline	4.73 <sup>27</sup>	1.96
4	4Me-aniline	5.08 <sup>27</sup>	1.96
5	2,3-Dimethyl aniline	4.64 <sup>27</sup>	1.54
6	2,4-Dimethyl aniline	5.00 <sup>27</sup>	1.64
7	2,5-Dimethyl aniline	4.60 <sup>28</sup>	1.83
8	2,6-Dimethyl aniline	4.10 <sup>27</sup>	1.54
9	3,4-Dimethyl aniline	5.22 <sup>29</sup>	2.00
10	2-Niroaniline	0.29 <sup>27</sup>	NA <sup>**</sup>
11	3-Niroaniline	2.47 <sup>27</sup>	NA <sup>**</sup>
12	4-Niroaniline	1.02 <sup>27</sup>	NA <sup>**</sup>
13	Piperidine	11.12 <sup>27</sup>	4.02
14	Morpholine	8.33 <sup>27</sup>	3.69
15	Quinoline	4.90 <sup>27</sup>	3.96
16	DMSO	-	1.76
17	Pyridine	5.20 <sup>10</sup>	4.41
18	2-Picoline	5.90 <sup>10</sup>	2.96
19	3-Picoline	5.68 <sup>10</sup>	4.3
20	4-Picoline	6.08 <sup>10</sup>	4.37
21	2,6-Lutidine	4.95 <sup>10</sup>	2.30
22	2,4-Lutidine	6.72 <sup>10</sup>	3.23
23	2,4,6-Collidine	7.48 <sup>27</sup>	3.13
24	2,2'-Bipyridyl	4.40 <sup>31</sup>	5.11
25	1,10-Phenanthroline	4.95 <sup>31</sup>	5.23
26	Ethylene diammine	6.84 <sup>31</sup>	5.20

\*\* NA - No adduct formation

For the adducts of Ni(DPC)<sub>2</sub> with aniline derivatives, viz., 3-methyl aniline, 4-methyl aniline, the K<sub>f</sub> values increases regularly with Pka. Were as in case of 2-methyl aniline, 2,3-dimethyl aniline, 2,4-dimethyl aniline, 2,5-dimethyl aniline and 2,6-dimethyl aniline there is a decrease in the stabilities of adducts

compared to aniline, this may be attributed to the steric hindrance offered by methyl group present in the 2-position, and hence these bases did not forms stable adducts.

The low values of logK<sub>f</sub> observed for Ni(DPC)<sub>2</sub> - aniline adducts may be attributed to the weak basic

character.<sup>24</sup> Thus it may be anticipated that the stronger the basic character the stronger will be the bonding in Ni(DPC)<sub>2</sub>-L adducts. Hence it may be concluded that Ni(DPC)<sub>2</sub> – pyridine adducts have stronger bonding than Ni(DPC)<sub>2</sub> – aniline adducts as it is evident from log K<sub>f</sub> values in Table 1.

Finally it should be noted that no systematic trend in the stability orders of pyridine, 3-picoline and 4-picoline are observed. On the other hand, the lower stabilities of 2-picoline, 2,4-lutidine, 2,6-lutidine and 2,4,6-collidine compared to pyridine may be attributed due to the steric hindrance caused by the methyl groups present at 2 and 6--position even though their pKa values are much more higher than pyridine.

The formation constant values for the morpholine and piperidine are not so high, this may be attributed to the decreased basicity of nitrogen atom in the ring. 4-picoline has higher stability constant value than 2-, 3-picolines, it is due to the higher pKa value and it does not possess any sterically hindering group.

It is surprising to find that the absorption spectrum of Ni(DPC)<sub>2</sub> does not change upon addition of 2-nitro aniline, 3-nitro aniline and 4-nitro aniline. This may be due to the fact that these nitrogen bases are very weak bases and hence do not form adducts with the Ni(DPC)<sub>2</sub> under these experimental conditions.

Bidentate bases such as bipyridyl, 1,10-phenanthroline and ethylenediamine forms stable complexes, in case of bidentate bases it appears that the adduct formation is not adversely influenced by the steric effects. This might be due to the rearrangement of chelate rings in order to provide a cis-position for bidentate adducting bases<sup>25</sup>.

## CONCLUSION

The reaction of various nitrogen bases with Ni(DPC)<sub>2</sub> under this investigation helps to improve our understanding about the structure of the nickel(II)diphenylcarbazonate. The behavior of these complexes is indicative of the tetrahedral configuration of nickel. In the investigation of stability constants of nickel(II)diphenylcarbazonate with various nitrogen bases, were planned to study the effect of basicity of nitrogen bases and steric hindrance on the stability of nickel(II)adducts. It was found that the stabilities of the adducts of nickel(II)diphenylcarbazonate chelate increases with increase in basicity of the bases and decrease with increase in steric hindrance. Furthermore the adduct formation constants for Ni(DPC)<sub>2</sub> are significantly higher than its sulphur analogue Ni(Dz)<sub>2</sub><sup>26</sup>, indicating that adducts of nickel chelates with O and N donor atoms prefer higher coordination number than four.

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