

Conformational Selectivity in the Diels–Alder Cycloaddition: Predictions for Reactions of *s-trans*-1,3-Butadiene

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Diels–Alder cycloaddition of *s-trans*-1,3-butadiene (**1**) should yield *trans*-cyclohexene (**7**), just as reaction of the *s-cis* conformer gives *cis*-cyclohexene (**9**). Investigation of this long-overlooked process with Hartree–Fock, Moller–Plesset, CASSCF, and DFT methods yielded in every case a C_2 -symmetric concerted transition state. At the B3LYP/6-31G* (+ZPVE) level, this structure is predicted to be 42.6 kcal/mol above reactants, while the overall reaction is endothermic by 16.7 kcal/mol. A stepwise diradical process has been studied by UBLYP/6-31G* theory and found to have barriers of 35.5 and 17.7 kcal/mol for the two steps. Spin correction lowers these values to 30.1 and 13.0 kcal/mol. The barrier to π -bond rotation in *cis*-cyclohexene (**9**) is predicted (B3LYP theory) to be 62.4 kcal/mol, with *trans*-cyclohexene (**7**) lying 53.3 kcal/mol above *cis* isomer **9**. Results suggest that π -bond isomerization and concerted reaction may provide competitive routes for Diels–Alder cycloreversion. It is concluded that full understanding of the Diels–Alder reaction requires consideration of both conformers of 1,3-butadiene.

Introduction

1,3-Butadiene exists in two minimum energy conformations, *s-trans* (**1**; Scheme 1) and *s-cis* (**2**), which differ in energy by ca. 3 kcal/mol.¹ Every discussion of the Diels–Alder reaction includes the observation that cycloaddition should occur only from the *s-cis* conformer to produce *cis*-cyclohexene (**9**). This conformational stereospecificity further implies that cycloaddition of *s-trans*-butadiene should lead to *trans*-cyclohexene (**7**). Nevertheless, the *s-trans* region of this potential surface has remained unexplored.

Early in the history of the Diels–Alder reaction, it was recognized that the higher energy *s-cis* conformer of butadiene presents the more favorable geometry for cycloaddition to give *cis*-cyclohexene (**9**).² This conformational preference has been supported by both theory and experiment. The C1–C4 distance in **1** is ca. 0.65 Å greater than in **2**. Thus, it is not surprising that, among the abundant literature on this famous reaction, the

reaction of the lower energy *s-trans* conformer seems to have been uniformly dismissed as impossible, and this often is cited as a textbook example of conformational selectivity.^{2h} In support of this idea, the effects of substituents on conformational bias in dienes and related cycloaddition rates have been investigated; reactivity diminishes with sterically demanding substituents at C2 or C3, and dienes with *trans* geometries fixed by ring fusion are unreactive.^{2,3} Other studies have shown that cycloaddition rates decrease with increasing C1–C4 distance.⁴ In keeping with the principle of microscopic reversibility, Diels–Alder cycloreversions are assumed to trace the opposite route.⁵ Much effort has focused on the question of concert in Diels–Alder cycloadditions; both theory and experiment provide evidence that a stepwise diradical mechanism lies only a few kcal/mol higher in energy than the concerted pathway.^{6–8}

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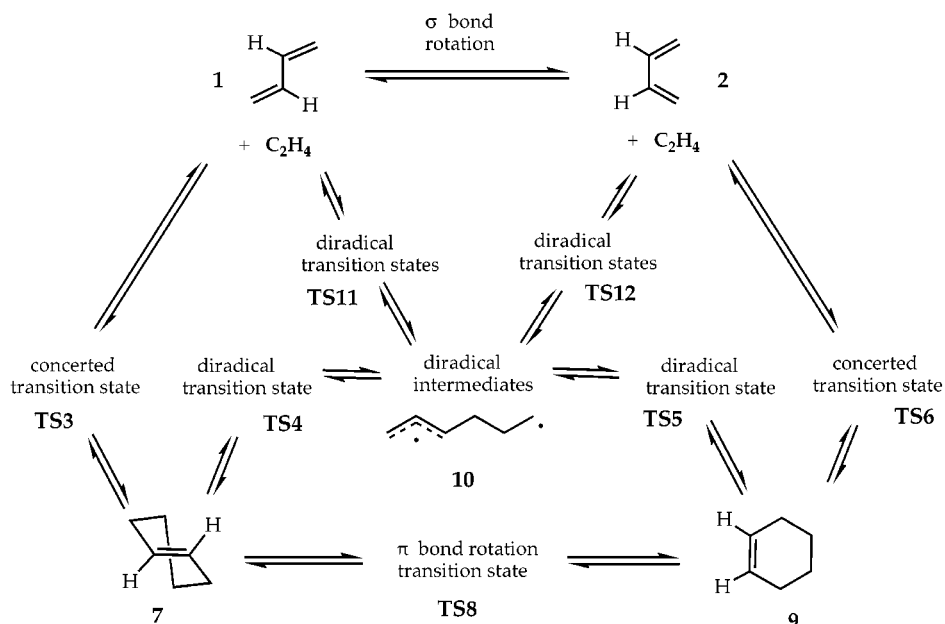
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Scheme 1. Potential Reactions of 1,3-Butadiene Conformers



The conventional view that limits Diels–Alder reactions to *s-cis* dienes clearly is too restrictive; enynes long have been studied as “diene” components,⁹ and we have recently shown that even 1,3-dienes can participate in cycloadditions to generate 1,2,3-cyclohexatrienes or benzyne.¹⁰ This context of high-energy product structures, as well compelling evidence for the formation of *trans*-cyclohexenes as transient products of photoisomerization,¹² led us to question whether concerted or stepwise reaction of *s-trans* conformer **1** could lead directly to **7**.¹¹ According to theory,¹³ the severely pyramidalized π bond in **7** destabilizes this substance by ca. 53 kcal/mol; nevertheless, the barrier for *trans* \rightarrow *cis* conversion remains ca. 10 kcal/mol,^{12g,13c} and several *trans*-cyclohexenes have been observed by flash photolysis. This implies the possibility of an alternate Diels–Alder mechanism in which cycloaddition of the more abundant *s-trans* conformer affords **7**, which then undergoes rapid π -bond isomerization to more stable **9**. While a significant contribution from the **1** + ethylene \rightarrow **7** \rightarrow **8** \rightarrow **9** pathway must be ruled out both by product strain and well-known stereochemical results,² the energetics and mechanism of this long-overlooked process remain unknown.

Simple analysis suggests that a reverse process passing through **7** may be more feasible. The experimental activation energy of 65–66 kcal/mol for the Diels–Alder cycloreversion of *cis*-cyclohexene¹⁴ is nearly identical to the π -bond rotational barrier in alkenes (ca. 65 kcal/mol).¹⁵ If cycloreversion of **7** were facile, this might provide an alternate mechanism for cycloreversion of **9**. Both concerted and diradical mechanisms have been considered previously.^{5,15} In addition, Lewis et al. have provided kinetic evidence for a very different mechanism passing through vinylcyclobutane.^{14c}

We present here the first discussion of comparative energetics for the Diels–Alder reaction of *both* conformers of butadiene. Our results help to answer longstanding textbook questions about the origin of conformational specificity in this archetypal pericyclic reaction and fill in an unknown, and intrinsically interesting, part of the potential surface.

Computational Methodology. Moller–Plesset¹⁶ and Beck3LYP¹⁷ calculations were carried out with Gaussian 98,¹⁸ while GaussView¹⁹ was used for visualization of

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Table 1. Computational Results for Diels–Alder Reactions

	E_{total} (au)	ZPVE (au)	entropy (eu)	$\langle S^2 \rangle$
Concerted Transition State TS3				
MP2(FC)/6-31G*	-233.653 52	0.142 86	75.2	
MP4SDTQ/6-31G*	-233.741 09			
B3LYP/6-31G*	-234.515 63	0.140 63	75.6	
CASSCF(6,6)/3-21G	-231.658 14	0.148 13	74.9	
TCSCF/6-31G*	-232.857 39	0.150 34	73.5	
pBP86/DN*	-234.580 66	0.134 03	77.8	
Diradical Transition State TS4				
UBLYP/6-31G*	-234.508 81	0.138 74	77.9	0.4678
TCSCF/6-31G*	-234.884 80	0.149 92	74.1	
Diradical Transition State TS11a				
UBLYP/6-31G*	-234.529 07	0.137 30	88.9	0.6058
Diradical Transition State TS11b				
UBLYP/6-31G*	-234.526 48	0.136 97	84.2	0.6337
Diradical Intermediate 10				
UBLYP/6-31G*	-234.535 57	0.137 27	86.0	1.0186
7				
MP2(FC)/6-31G*	-233.706 58	0.148 54	70.9	
MP4SDTQ/6-31G*	-233.797 20			
B3LYP/6-31G*	-234.561 90	0.145 62	71.5	
pBP86/DN*	-234.620 01	0.138 83	73.3	
π -Bond Transition State TS8				
UB3LYP/6-31G*	-234.543 60	0.141 85	72.4	0.9972
<i>s-cis</i> -1,3-butadiene (2)				
B3LYP/6-31G*	-155.986 49	0.085 34	66.7	

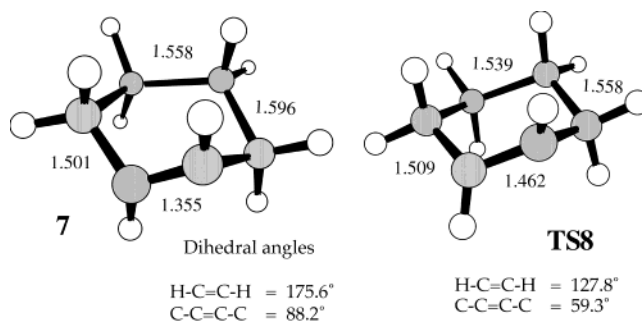
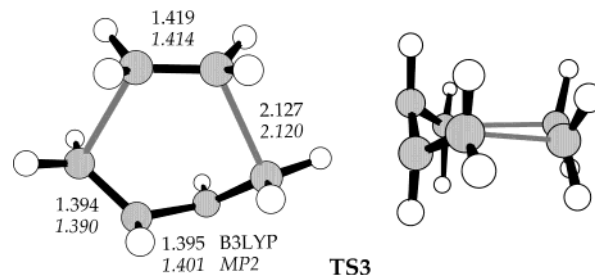
Table 2. Energy Differences (kcal/mol) between *cis* (TS6) and *trans* (TS3) Transition States

MP2(FC)/6-31G*	16.1
MP4SDTQ/6-31G*	17.0
B3LYP/6-31G*	17.7
CASSCF(6,6)/3-21G	19.7
pBP86/DN*	16.3

these results. TCSCF and CASSCF calculations employed the Macintosh version of GAMESS,²⁰ with MacMolplot²¹ used for visualizations. Hartree–Fock and pBP86 DFT calculations were performed with Spartan.²² In every case, Hessian analysis was used to characterize stationary points. Gaussian 98 was used to calculate transition-state magnetic properties using the GIAO method.²³

Results and Discussion

***trans*-Cyclohexene (7).** Previous theoretical studies have located two conformers of *trans*-cyclohexene (**7**).¹³ The lower energy conformer resembles the chair structure of cyclohexane. To assess its energetics, **7** was optimized with MP2 and DFT methods. Additionally, the π -bond rotation transition state (**TS8**) for cyclohexene was located with a UBLYP/6-31G* wave function. Model calculations show that this level of theory slightly underestimates the rotational barrier in ethylene.^{15,24} Numerical results are summarized in Tables 1 and 2, while Figure 1 shows selected geometric parameters for **7**, which are similar to previous results.¹³ Despite its unusual geometry and strain, the unscaled B3LYP/6-

**Figure 1.** B3LYP/6-31G(d)-optimized structures for **7** and the cyclohexene π -bond rotation transition state.**Figure 2.** Transition-state structure for concerted cycloaddition of *s-trans*-1,3-butadiene.

31G* double bond vibrational frequency for **7** is an unremarkable 1614 cm^{-1} .

DFT theory appears to do an excellent job on singlet diradicals. Spin contamination in unrestricted DFT methods is much less pronounced than with UHF theories; nevertheless, Yamaguchi and co-workers have suggested a correction for this problem.²⁵ Following this method as described by Houk and co-workers,^{6c} spin correction lowers the predicted rotational barrier by a modest 0.9 kcal/mol. Our predicted *trans* \rightarrow *cis* barrier of 9.1 kcal/mol (8.2 with spin correction) is slightly lower than the experimental value for phenylcyclohexene that was measured by Caldwell¹² or with previous estimates based on TCSCF calculations.¹³ *trans*-Cyclohexene is consistently predicted to be ca. 53 kcal/mol less stable than *cis*. It is surprising that this *cis*–*trans* isomerization barrier in cyclohexene is nearly identical to that predicted for ethylene. This probably reflects the fact that product strain and π -bond isomerization have identical origins.

Two New Diels–Alder Transition States. The central question posed here is what reaction paths connect **1** + ethylene with **7**. As a first step, the transition state (**TS3**) leading to **7** by concerted cycloaddition was located, first at the HF/3-21G level, with constraint to C_2 symmetry. Attempts to find a second transition state leading to the higher energy conformation of **7** led to this same structure. Further optimizations of transition state **TS3** with an assortment of wave functions resulted in similar C_2 -symmetric structures; in every case, Hessian analysis yielded a single imaginary vibrational mode. Numerical results are summarized in Tables 1 and 2,

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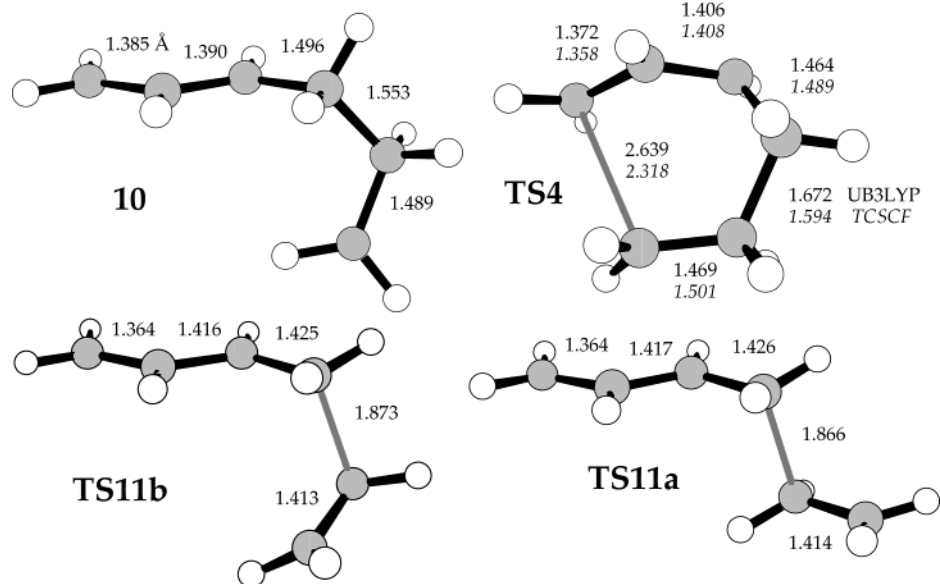


Figure 3. Stationary points on the diradical route to *trans*-cyclohexene.

while Figure 2 shows MP2 and B3LYP geometric parameters. The transition-state structure resembles Möbius benzene (*trans*, *cis*, *cis*-1,3,5-cyclohexatriene), a structure we recently characterized as a shallow minimum on the C_6H_6 potential surface.²⁶ However, the present orbital topology should be Hückel; all computational results are consistent with a $[\pi 2s + \pi 4s]$ process.²⁷ Table 2 summarizes energy differences for the two concerted transition states. On the basis of previous results for Diels–Alder reactions,^{6,28} MP4 and B3LYP energies should provide the most accurate predictions.

This concerted pathway must have a multistep counterpart of similar energy. Initial bond formation would give diradical **10**, one conformer of which has a suitable geometry for closure to **7**. It seemed most appropriate to work backward from **7**; thus, the transition state (**TS4**) for the second step in this diradical route to **7** was first located with both TCSCF/6-31G* and UBLYP/6-31G* wave functions. Selected geometric parameters are given in Figure 3. The intrinsic reaction coordinate was also calculated with a TCSCF wave function and showed a smooth transformation from **TS4** to a diradical structure (**10**) in one direction and to **7** in the other. Previous attempts to locate a similar transition state for final closure in the reaction of **2** were reported to be unsuccessful, presumably because the barrier is very low.^{6c} The structure of the diradical intermediate **10** was then further optimized with the same UBLYP wave function, as were two transition states (**TS11a** and **TS11b**) for the addition of ethylene to diene conformation **1**. **TS11b** maintains the same *gauche* conformation as **10**; thus, the sequence **1** + ethylene → **TS11b** → **10** → **TS4** → **7** should provide a complete stepwise profile. Spin corrections^{6c,25} (Table 3) were found to lower the diradical transition-state energies by ca. 5 kcal/mol.

Table 3 summarizes the BLYP/6-31G* energetics for Diels–Alder reactions of both butadiene conformers. This

Table 3. B3LYP/6-31G* Relative Energies and Entropies of Stationary Points^{a,b}

structure	E_{rel} (kcal/mol) B3LYP/6-31G*	ΔS_{rel} (eu)
Diels–Alder Cycloadditions		
1 + ethylene	0.0	0.0
2 + ethylene	3.46	0.7
concerted <i>cis</i> TS6	24.8 ^c	−40.6 ^c
concerted <i>trans</i> TS3	42.6	−42.7
<i>cis</i> -cyclohexene (9)	−36.6 ^c	−45.9 ^c
<i>trans</i> -cyclohexene (7)	16.7	−46.8
diradical TS11a	32.1 (26.5)	−29.4
diradical TS11b	35.5 (30.1)	−34.1
intermediate 10	28.0 (27.5)	−32.3
second diradical TS4	45.7 (40.5)	−40.4
π -Bond Rotation		
<i>cis</i> -Cyclohexene (9)	0.0	0.0
π bond TS8	62.4 (61.5)	0.0
<i>trans</i> -cyclohexene (7)	53.3	−0.9
Cycloreversion of <i>cis</i> -Cyclohexene (9)		
concerted TS6	61.4	5.3
Cycloreversion of <i>trans</i> -Cyclohexene (7)		
concerted TS3	25.9	4.1
diradical TS4	29.0 (23.8)	6.4

^a ZPVE corrections are included in all cases. ^b Numbers in parentheses are after spin correction. ^c Data from ref 6c.

level of theory can be consistently applied for all mechanistic steps and provides values that agree well with available experimental data.^{6,28} Data for the formation of **9** are from similar calculations by Houk and co-workers.^{6c} Predictably, the energetics for reactions of conformers **1** and **2** are strikingly different. Without considering entropy changes, stereospecific cycloadditions of conformers **1** and **2** are predicted to be *endothermic* by 16.7 kcal/mol and *exothermic* by 36.6 kcal/mol, respectively. Nevertheless, the difference between the two concerted transition states is only 16–18 kcal/mol; this is one-third of the energy difference between the two stereoisomeric products. Aside from the partially formed *trans* π bond, the major geometric difference between concerted transition structures **TS3** and **TS6** is that the nascent σ bond is ca. 0.15 Å *shorter* in the *trans* transition state. This is ascribed to the more product-like character of this endothermic reaction. Consistent with the long-

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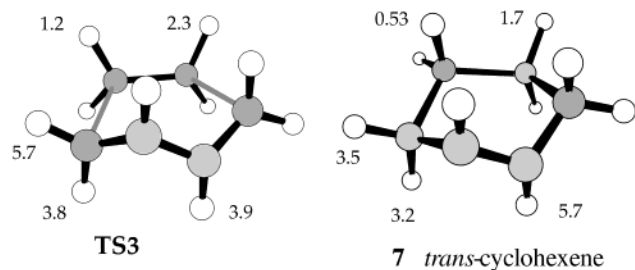


Figure 4. B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) GIAO chemical shifts (ppm relative to TMS).

held skepticism for reaction of **1**, this transition state must be destabilized because the ends of the diene are too far apart, which results in twisting of the nascent central π bond. The entropic difference between the two transition states is modest and does not alter these conclusions. While a concerted reaction is thus possible for both conformers of 1,3-butadiene, the relative energetics ensure that essentially all of the chemistry must derive from the *cis* diene.

As with the well-studied *cis* cycloaddition, a stepwise mechanism is predicted to have similar energetics. Addition to **1** with ethylene through **TS11b** has a barrier of 35.5 kcal/mol (30.1 kcal/mol with spin correction). This leads to **10** as a shallow minimum, followed by a second barrier of 17.7 kcal/mol (13.0 kcal/mol with spin correction) for closure to **7** through **TS4**. **TS11a** provides a slightly lower energy for the initial addition; this would be followed by a conformational change to reach **10**. The potential surfaces for diradical **10** must be complex; this can dissociate to reactants, close to **7**, or close to vinylcyclobutane.^{14c} Overall, it seems that stepwise addition of ethylene can occur to either diene conformer with similar facility to afford a collection of diradical intermediates. However, barriers to interconversion or closure probably are lower than those for scission to reactants. Detailed dynamic studies would be necessary to understand the competition among these processes. Closure to **7** by this route is precluded by the high barrier in this second step.

Magnetic Properties of the Concerted Transition State. Schleyer and co-workers have shown that the expected aromaticity of transition states can be elegantly demonstrated by direct calculation of magnetic properties.²⁹ Because transition state **3** describes a [$\pi 2s + \pi 4s$] array, it should be aromatic. Figure 4 shows ¹H NMR chemical shifts calculated at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G* level of theory for the transition state and product. The most dramatic effect is seen in the equatorial hydrogen of the incipient allylic group. The chemical shift of δ 5.8 is ca. 1 ppm downfield relative to **1**, which is consistent with an aromatic transition state.

Mechanism of the Retro-Diels–Alder Reaction. The substantial exothermicity of Diels–Alder cycloadditions results in a large barrier for cycloreversion. Nevertheless, retro-Diels–Alder reactions have been widely investigated and used in synthesis.^{2,5,14} Zewail recently studied the femtosecond time scale cycloreversion of norbornene and concluded that diradical and concerted mechanisms are both operative.⁷ Photochemical retro-Diels–Alder reactions are well-known.^{5,30} One of our initial questions was whether these photoreactions might proceed by initial *cis*–*trans* isomerization, followed by cycloreversion of **7**. Given our present results, this seems unlikely because the barrier to *trans*–*cis* isomerization is >10 kcal/mol lower than that for cycloreversion.

The experimental activation energy for thermal cleavage of cyclohexene is 65–66 kcal/mol.^{5,14} Using data from Houk and co-workers,^{6c} concerted cycloreversion of **9** is predicted to have a barrier of 61.4 kcal/mol, slightly lower than the experimental value. According to our calculations, π -bond rotation has a predicted barrier of 62.4 kcal/mol (61.5 kcal/mol with spin correction). Both numbers would be improved by higher level calculations, but their similarity suggests that *cis*–*trans* isomerization in cyclohexene might occur in competition with cycloreversion! This also provides a previously unrecognized indirect route for cycloreversion via **7**. Cycloreversions of **7** or **9** should have opposite stereochemical consequences in the diene component; thus, this question may be subject to experimental verification. The stereochemistry of the diene fragment in the Diels–Alder cycloreversion of simple cyclohexenes has not been described.⁵

Conclusions

The Diels–Alder cycloaddition is stereospecific with respect to conformation. Concerted and stepwise reaction paths exist for both *cis* and *trans* diene conformers which connect them to the respective isomers of cyclohexene. Energetics of the *s*-*trans* reaction are unfavorable because of product strain. Nevertheless, our results demonstrate for the first time that the usual paradigm for Diels–Alder reactions is incomplete: a thorough understanding of this archetypal reaction requires consideration of the *full* range of processes shown in Scheme 1, not just those involving the *s*-*cis* conformer.

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Supporting Information Available: Tables of Cartesian coordinates for stationary points. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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