

Cis and Trans Isomers of Cycloalkenes

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This article is one of a series in which we explore the structural and electronic consequences of various deformations of alkenes.¹ In particular, this article examines the strain in medium-sized cycloalkenes and the geometric and electronic distortions through which alkenes can relieve that strain. This topic is explored in many variations at different levels in organic chemistry and computational chemistry courses (1, 2). In this article, we summarize literature data and present the results of our theoretical examination of medium-sized cycloalkenes. Our goal is to provide a concise reference for those interested in addressing this topic in an introductory organic chemistry curriculum. A companion article presents a molecular modeling laboratory exercise that allows students to explore cis and trans cycloalkenes in a guided-inquiry fashion (3).

Results

Relative Energies of the Cis and Trans Isomers

The calculated energies (E) at various levels of theory and zero-point energy (ZPE) correction of each pair of cycloalkene isomers are listed in Table 1. Table 2 compiles these data into a series of $\Delta\Delta_f H$ values (kcal/mol), where

$\Delta\Delta_f H = \Delta_f H_{\text{trans}} - \Delta_f H_{\text{cis}} = E_{\text{trans}} - E_{\text{cis}}$. Positive-valued entries imply that the cis isomer is more stable than the trans isomer. Columns 5 and 7 include the ZPE corrections. Table 3 contains the experimental $\Delta\Delta_{\text{hyd}} H$ values from hydrogenation data (abbreviated as hyd) and from solution equilibrium data. Note that for hydrogenation, $\Delta\Delta_{\text{hyd}} H = \Delta_{\text{hyd}} H_{\text{cis}} - \Delta_{\text{hyd}} H_{\text{trans}} = \Delta\Delta_f H$; entries are placed in the row for the trans isomer. (No experimental data are available for the $\Delta_{\text{hyd}} H$ of *trans*-cycloheptene.) Both experimentally and computationally, cis cycloalkenes are more stable than trans cycloalkenes for ring sizes of ten or fewer members.

For the most part, the magnitude of the energy difference between cis and trans becomes smaller and smaller as one moves to larger and larger ring sizes. Only one exception to this trend is seen in experimental observations and is only reproduced with the LMP2 method: $\Delta_{\text{rxn}} H$ for isomerization (trans \rightarrow cis) is slightly greater in magnitude for the cyclododecenes than for the cyclononenes (Table 2). The explanation presented for this surprising observation is based on solvent effects that should favor *cis*-cyclododecene over the trans isomer more than *cis*-cyclononene is favored over its trans isomer (4). However, calculations that include solvation effects do not support this argument.²

Table 1. Absolute Energies of Cis and Trans Cycloalkenes

Cycloalkene	AM1/ (kcal/mol)	HF/cc-pVTZ Energy/hartree	LMP2/cc-pVTZ Energy/hartree	B3LYP/cc-pVTZ Energy/hartree	Zero-Point Energy/(kcal/mol)
<i>cis</i> -Cycloheptene	-14.142	-272.129 81	-273.189 82	-274.047 28	109.642
<i>trans</i> -Cycloheptene	16.764	-272.073 89	-273.145 42	-273.999 56	109.147
<i>cis</i> -Cyclooctene	-18.120	-311.170 19	-312.389 28	-313.368 89	127.893
<i>trans</i> -Cyclooctene	-5.905	-311.148 24	-312.372 19	-313.350 76	127.511
<i>cis</i> -Cyclononene	-23.381	-350.209 84	-351.586 32	-352.689 89	145.951
<i>trans</i> -Cyclononene	-18.429	-350.201 67	-351.581 17	-352.683 27	145.677
<i>cis</i> -Cyclododecene	-29.948	-389.259 18	-390.792 23	-392.019 32	164.093
<i>trans</i> -Cyclododecene	-28.650	-389.252 12	-390.786 09	-392.013 24	163.569
<i>cis</i> -Cycloundecene	-37.851	-428.304 64	-429.994 68	-431.342 08	181.779
<i>trans</i> -Cycloundecene	-38.598	-428.306 28	-429.996 02	-431.346 30	181.716

Table 2. Relative Energies of the Cycloalkene Isomers

Ring Size	$\Delta\Delta_f H$ /(kcal/mol)					
	AM1	HF/cc-pVTZ	LMP2/cc-pVTZ	LMP2/cc-pVTZ with ZPE	B3LYP/cc-pVTZ	B3LYP/cc-pVTZ with ZPE
7	30.9	35.1	27.9	27.4	29.9	29.4
8	12.2	13.8	10.7	10.3	11.4	11.0
9	5.0	5.1	3.2	3.0	4.2	3.9
10	1.3	4.4	3.8	3.3	3.8	3.3
11	-0.7	-1.0	-0.8	-0.9	-0.6	-0.7

Experimentally, it has been found that for rings of 11 or more members trans cycloalkenes are more stable³ than cis. Consistent with the experimental findings, each computational method used here predicts a slight preference for the *trans*-cycloundecene isomer.

Geometry: Overview

It has been found that when a comparison can be made, the minimum-energy conformers reported and pictured in Figure 1 are consistent with experimentally determined structures (5). To determine the lowest-energy conformer a conformational-analysis calculation was performed for each isomer at the AM1 level and the lowest two or three conformers were then optimized at higher levels.

Careful examination of the trans cycloalkene isomers of 7–10 members reveals four types of geometric nonideality that are not found in the cis isomer:

- twisted π bonds,
- pyramidal sp^2 -carbon atoms,
- nonideal sp^3 bond angles, and
- longer than normal C–C bonds (cycloheptene and cyclooctene only).

Geometry: Specifics

Twist angle (T) at a C=C double bond (Figure 2) can be defined as the angle between the plane defined by C1, Cn, and H (on C1) and the plane defined by C2, C3, and H (on C2). This angle is straightforward to conceptualize (as seen in Figure 2) when only rotation about the C=C double bond is considered.¹ However, twisting in the trans cycloalkenes (ring size 7–9) is accompanied by pyramidalization (6, 7), and pyramidalization renders “twist angle” as defined above somewhat meaningless. A more useful definition, p-orbital misalignment, will be given later.¹

Pyramidalization angle (Φ) is illustrated in Figure 2. Two values are given as a measure of the degree of pyramidalization. The first measurement of pyramidalization,

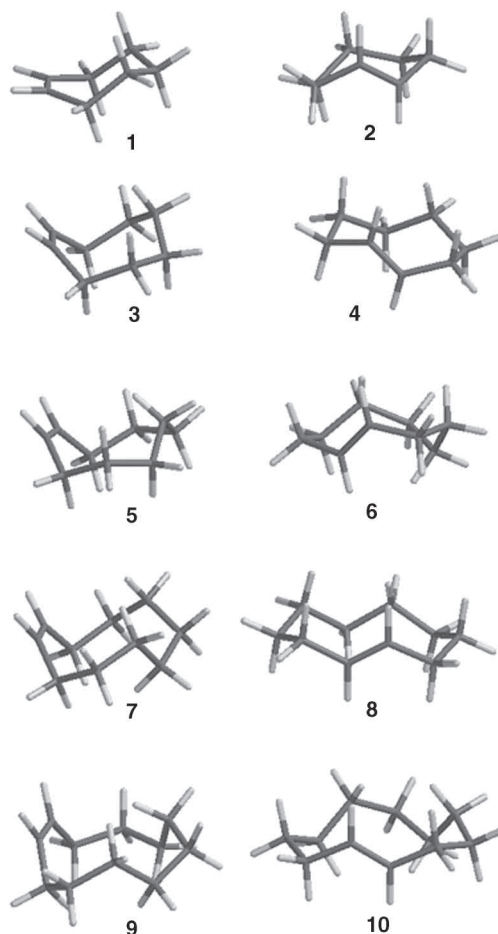


Figure 1. Models of the minimum-energy conformers. Cycloalkenes are pictured in order of increasing size from top to bottom. The odd-numbered models are the cis isomers and the even-numbered models are the trans isomers.

Table 3. Experimental ΔH of Hydrogenation and Relative $\Delta\Delta_f H$ Values of Cis and Trans Cycloalkenes

Cycloalkene	$\Delta_{\text{hyd}}H/$ (kcal/mol) ^a	$\Delta\Delta_f H/$ (kcal/mol) ^b	$\Delta\Delta_f H/$ (kcal/mol) ^c
<i>cis</i> -Cycloheptene	-25.85	—	—
<i>trans</i> -Cycloheptene	—	—	—
<i>cis</i> -Cyclooctene	-22.98	—	—
<i>trans</i> -Cyclooctene	-32.24	9.26	—
<i>cis</i> -Cyclononene	-23.62	—	—
<i>trans</i> -Cyclononene	-26.49	2.87	2.9 (2.9)
<i>cis</i> -Cyclodecene	-20.67	—	—
<i>trans</i> -Cyclodecene	-24.01	3.34	3.6 (3.3)
<i>cis</i> -Cycloundecene	—	—	—
<i>trans</i> -Cycloundecene	—	—	-0.12 (-0.12)

^aExperimental values (4b).

^bValues from from $\Delta_{\text{hyd}}H$ (4a).

^cValues from acetic acid solution equilibrium (4c).

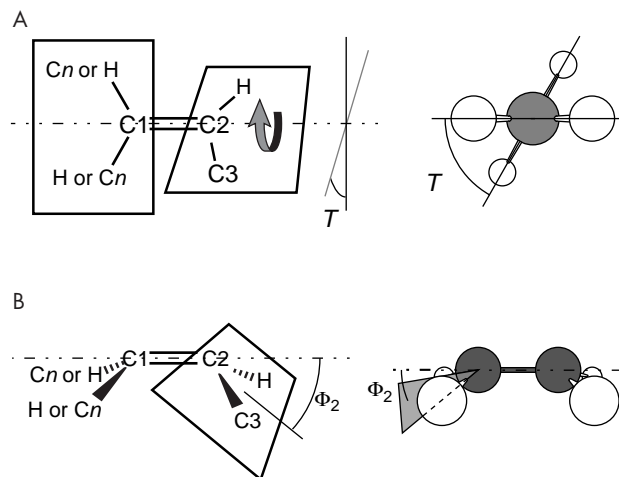


Figure 2. Angles defined as (A) twist angle T and (B) pyramidalization angle Φ_2 . Ball-and-stick models of ethene illustrate T and Φ_2 . In A the plane containing C1 and its two attached hydrogen atoms is in the foreground, eclipsing C2. The twist angle in the ball-and-stick model is 60° .

Φ_1 , is equal to $360^\circ - \sum$ (bond angles surrounding sp^2 carbon) (8, 9).⁴ The second measurement of pyramidalization, Φ_2 , corresponds to the angle between the C1–C2 axis and the H–C1–C_n plane for C1, and to the angle between the C1–C2 axis and the H–C2–C3 plane for C2.

The twisting of the π bond in the *trans* cycloalkenes occurs such that the allylic carbons are brought closer together. This compensates for the shorter than ideal $(CH_2)_n$ tether available for linking the allylic carbons in the *trans* positions of the double bond. Note also that the dihedral angle H–C1=C2–H remains very close to 180° , regardless of how great the deviation from 180° is for the C_n–C1=C2–C3 dihedral angle.

Twisting decreases, predictably, as ring size increases from *trans*-cycloheptene to *trans*-cycloundecene (Table 4). Note that the calculated allylic carbon dihedral angles (C_n–C1=C2–C3) can be used to quantify the extent of twisting of the C=C double bond. As the degree of twisting decreases so does pyramidalization. Pyramidalized sp^2 carbons are clearly evident in *trans*-cycloheptene, but are barely noticeable in *trans*-cyclodecene and *trans*-cycloundecene. Values for both definitions of pyramidalization appear in Table 4. Note that Φ_1 values are substantially smaller than Φ_2 values.

Table 4. Dihedral Angles and Degrees of Pyramidalization, Φ , in *Trans* Cycloalkenes Calculated at B3LYP/cc-pVTZ Level

Cycloalkene	C=C=C Dihedral Angle/deg ^a	Φ_1 /deg	Φ_2 /deg
<i>cis</i> -Cycloheptene	0.0 (0.0)	0.01, 0.01	0.87, 0.87
<i>cis</i> -Cyclooctene	2.2 (2.2)	0.01, 0.10	0.89, 2.98
<i>cis</i> -Cyclononene	4.2 (4.2)	0.00, 0.13	0.12, 3.38
<i>cis</i> -Cyclodecene	0.5 (0.5)	0.00, 0.02	0.44, 1.21
<i>cis</i> -Cycloundecene	3.8 (3.8)	0.02, 0.03	1.08, 1.62
<i>trans</i> -Cycloheptene	116.3 (63.7)	8.39, 9.23	28.14, 29.55
<i>trans</i> -Cyclooctene	136.9 (42.11)	3.76, 3.79	18.74, 18.74
<i>trans</i> -Cyclononene	149.0 (31.0)	1.82, 1.82	12.97, 12.97
<i>trans</i> -Cyclodecene	167.9 (12.1)	0.18, 0.30	5.20, 5.21
<i>trans</i> -Cycloundecene	175.8 (4.2)	0.03, 0.03	1.68, 1.70

^aIn parentheses is the degrees twisted from the ideal angle.

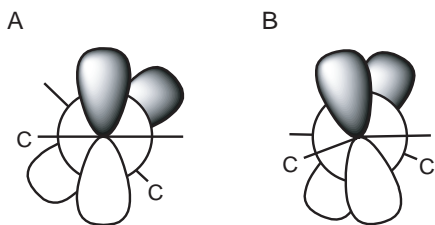


Figure 3. Newman projections demonstrating: (A) a pure twisting of the π bond and (B) twisting with pyramidalization. In each case, the dihedral angle between allylic carbons is 135° , but p-orbital overlap is greater in B (10). Note also that the hydrogen atoms attached to the sp^2 carbons remain nearly aligned (H–C=C–H dihedral angle $\sim 180^\circ$) in B (7, Boggs).

The combination of twisting and pyramidalization in a C=C double bond is illustrated in Figure 3. This figure shows the reason why twisting is accompanied by pyramidalization: It helps to maximize p-orbital overlap (10). Figure 4 provides an end-on view of the π bond in the fully optimized geometry (left) in *trans*-cyclooctene in comparison with a molecular geometry in which the sp^2 -carbon atoms are constrained to planarity (right). In addition to maintaining p-orbital overlap in the π bond, pyramidalization also occurs in a direction that relieves torsional repulsions (Figure 5) (11).

HOMOs of *Trans* Cycloalkenes

The trend that can be quickly recognized is an increase in π -bond distortion as ring size decreases across the series (Figure 6). There is a sizable increase in the lobe outside of the ring and twist of one lobe with respect to the other.⁵ Examination of certain other strained alkenes, cubene, for example, indicates that pyramidalization of the sp^2 -carbon atoms alone can cause the unsymmetrical distribution of the π electron density. According to Fukui, extensive σ -to- π bond mixing causes the unsymmetrical distribution of the π electron density on both faces of the double bond, an effect he termed “nonequivalent orbital extension” (12).

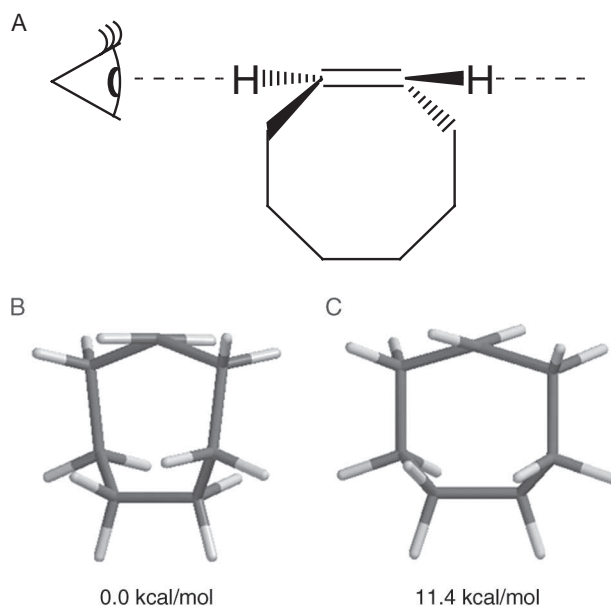


Figure 4. (A) The perspective from which the cyclooctene models are viewed. (B) Optimized *trans*-cyclooctene geometry. (C) Geometry with twisting allowed but sp^2 carbons constrained planar. The absolute energies are -313.35075 hartrees in B and -313.33251 hartrees in C.

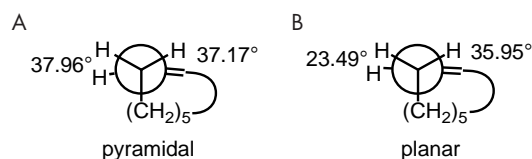


Figure 5. Newman projections looking toward the double bond from an allylic carbon in the optimized (A) *trans*-cyclooctene structure (pyramidal) and the (B) *trans*-cyclooctene structure with constrained planarity of the sp^2 carbons.

Bond Angles

Table 5 lists each C(sp^x)-C(sp³)-C(sp³) bond angle found in cyclic alkenes studied here ($x = 2$ or 3). Bond-angle values in the trans isomers are much more varied than in the cis isomers. Except for bond angles centered on the allylic carbons ($x = 2$), the calculated bond angles are larger than the ideal 109.5°.⁶ Of the cycloalkenes studied here, the largest bond angle is found in *trans*-cyclononene. The bond angles centered on the allylic carbons in *trans*-cycloheptene, -octene, and -nonene are smaller than the ideal, with the smallest bond angle of 103.70° found in *trans*-cycloheptene. The small bond angles at these positions in the rings serve two purposes. First, a “quick” bend is required to decrease the length needed to reconnect the two ends of a double bond via its trans positions. Second, a small bond angle seems to increase the hyperconjugative interaction between the C-C σ bonds and LUMO (Figure 7).

Bond Lengths

It would be reasonable to hypothesize that we might see an increase in C-C bond lengths in the smaller-sized trans molecules to accommodate the distance needed to connect the allylic carbons via the (CH₂)_{*n*} tether. However, *trans*-cycloheptene exhibits a large range of bond lengths. The short-

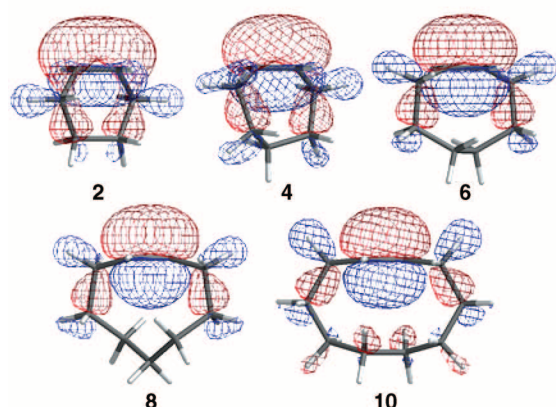


Figure 6. HOMOs of *trans*-cycloheptene **2**, *trans*-cyclooctene **4**, *trans*-cyclononene **6**, *trans*-cyclodecene **8**, and *trans*-cycloundecene **10**. Each ring is oriented such that the upper lobe (outside of the ring) of the HOMO is contained in the plane of the page, with the lower lobe (inside of the ring) is twisted out of the plane. This twisting is much more easily seen by examining the models in the Supplemental Material.¹¹

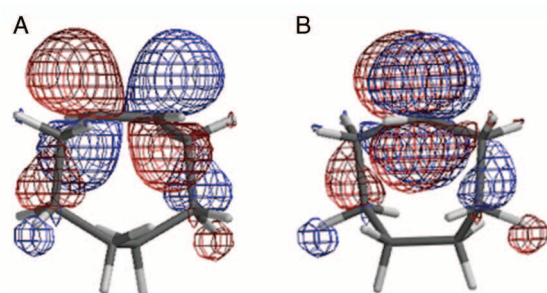


Figure 7. (A) Side view and (B) end view of the LUMO of *trans*-cyclooctene illustrating the possibility of enhanced hyperconjugative interactions.

est C-C bond in the optimized geometry of *trans*-cycloheptene is 1.498 Å, while the longest is 1.576 Å. Similarly, the shortest and longest bond lengths in *trans*-cyclooctene are 1.493 Å and 1.565 Å, respectively. Note that the vinylic C-C bonds are always the shortest of the single bonds in any of the cycloalkenes, and are shorter in the trans isomer than the cis. The vinylic bonds in *trans*-cycloheptene through *trans*-cyclononene are significantly shorter than their counterparts in the cis isomer. It appears that the shorter than normal vinylic bond serves to decrease the length of the sp³ carbon tether needed to reconnect the double bond.⁷ In Table 6 the calculated bond lengths of each C-C single bond are listed. The average bond length (with vinylic bond excluded) in-

Table 5. Bond Angles Centered on sp³ Carbons

<i>cis</i> -Cycloheptene		<i>trans</i> -Cycloheptene	
(C2-C3-C4)	115.75 (113.98)	(C2-C3-C4)	103.70 (103.70)
(C3-C4-C5)	115.19 (114.22)	(C3-C4-C5)	117.29 (116.77)
(C4-C5-C6)	115.81 (115.76)	(C4-C5-C6)	119.51 (118.88)
(C5-C6-C7)	115.19 (114.22)	(C5-C6-C7)	116.69 (116.07)
(C6-C7-C1)	115.75 (113.98)	(C6-C7-C1)	102.02 (101.44)
<i>cis</i> -Cyclooctene		<i>trans</i> -Cyclooctene	
(C2-C3-C4)	115.22 (112.01)	(C2-C3-C4)	105.78 (105.08)
(C3-C4-C5)	117.10 (114.67)	(C3-C4-C5)	115.87 (114.96)
(C4-C5-C6)	116.75 (115.77)	(C4-C5-C6)	118.54 (118.25)
(C5-C6-C7)	116.50 (116.26)	(C5-C6-C7)	118.54 (118.25)
(C6-C7-C8)	115.76 (116.35)	(C6-C7-C8)	115.87 (114.96)
(C7-C8-C1)	113.15 (114.59)	(C7-C8-C1)	105.78 (105.08)
<i>cis</i> -Cyclononene		<i>trans</i> -Cyclononene	
(C2-C3-C4)	116.89 (116.49)	(C2-C3-C4)	108.06 (106.81)
(C3-C4-C5)	116.12 (115.79)	(C3-C4-C5)	114.54 (113.72)
(C4-C5-C6)	117.56 (116.67)	(C4-C5-C6)	117.98 (116.90)
(C5-C6-C7)	119.22 (118.16)	(C5-C6-C7)	121.26 (119.35)
(C6-C7-C8)	117.54 (116.52)	(C6-C7-C8)	117.98 (116.90)
(C7-C8-C9)	116.19 (115.61)	(C7-C8-C9)	114.54 (113.72)
		(C8-C9-C1)	108.06 (106.81)
<i>cis</i> -Cyclodecene		<i>trans</i> -Cyclodecene	
(C2-C3-C4)	114.12 (113.48)	(C2-C3-C4)	112.91 (111.87)
(C3-C4-C5)	118.00 (117.26)	(C3-C4-C5)	116.24 (115.66)
(C4-C5-C6)	118.17 (117.16)	(C4-C5-C6)	115.42 (115.23)
(C5-C6-C7)	117.34 (116.72)	(C5-C6-C7)	115.11 (114.62)
(C6-C7-C8)	114.63 (114.17)	(C6-C7-C8)	115.11 (114.65)
(C7-C8-C9)	114.97 (114.25)	(C7-C8-C9)	115.42 (115.25)
(C8-C9-C10)	114.50 (113.56)	(C8-C9-C10)	116.24 (115.66)
(C9-C10-C1)	113.85 (113.04)	(C9-C10-C1)	112.91 (111.91)
<i>cis</i> -Cycloundecene		<i>trans</i> -Cycloundecene	
(C2-C3-C4)	112.97 (112.39)	(C2-C3-C4)	114.55 (113.64)
(C3-C4-C5)	114.45 (113.59)	(C3-C4-C5)	114.12 (113.33)
(C4-C5-C6)	114.92 (114.29)	(C4-C5-C6)	114.55 (114.63)
(C5-C6-C7)	113.85 (113.36)	(C5-C6-C7)	114.13 (113.21)
(C6-C7-C8)	113.49 (112.75)	(C6-C7-C8)	113.48 (112.64)
(C7-C8-C9)	113.89 (113.28)	(C7-C8-C9)	114.13 (113.21)
(C8-C9-C10)	115.39 (115.14)	(C8-C9-C10)	114.55 (114.64)
(C9-C10-C11)	114.79 (114.14)	(C9-C10-C11)	114.12 (113.33)
(C10-C11-C1)	116.57 (115.89)	(C10-C11-C1)	114.55 (113.64)

NOTE: Angles (in degrees) are calculated at B3LYP and LMP2/cc-pVTZ levels. LMP2 values in parentheses.

Table 6. C-C Single Bond Lengths in Cycloalkenes

Bond	<i>cis</i> -Cycloheptene (Å)	<i>trans</i> -Cycloheptene (Å)
C2-C3	1.510 (1.510)	1.498 (1.500)
C3-C4	1.538 (1.539)	1.565 (1.563)
C4-C5	1.532 (1.534)	1.560 (1.559)
C5-C6	1.532 (1.533)	1.566 (1.567)
C6-C7	1.539 (1.539)	1.576 (1.568)
C7-C1	1.510 (1.510)	1.503 (1.504)
Average 1.535 Å		Average: 1.567 Å
Average difference: 0.032 Å		
<i>cis</i> -Cyclooctene (Å)	<i>trans</i> -Cyclooctene (Å)	
C2-C3	1.502 (1.503)	1.493 (1.493)
C3-C4	1.544 (1.542)	1.558 (1.553)
C4-C5	1.537 (1.533)	1.549 (1.546)
C5-C6	1.545 (1.542)	1.565 (1.558)
C6-C7	1.540 (1.558)	1.549 (1.546)
C7-C8	1.544 (1.543)	1.558 (1.553)
C8-C1	1.510 (1.509)	1.493 (1.493)
Average: 1.542		Average 1.556
Average difference: 0.014 Å		
<i>cis</i> -Cyclononene (Å)	<i>trans</i> -Cyclononene (Å)	
C2-C3	1.511 (1.504)	1.495 (1.496)
C3-C4	1.552 (1.546)	1.554 (1.551)
C4-C5	1.548 (1.538)	1.550 (1.550)
C5-C6	1.538 (1.539)	1.544 (1.541)
C6-C7	1.535 (1.547)	1.544 (1.541)
C7-C8	1.535 (1.536)	1.550 (1.550)
C8-C9	1.549 (1.542)	1.554 (1.551)
C9-C1	1.501 (1.506)	1.495 (1.496)
Average 1.543		Average 1.549
Average difference: 0.006 Å		
<i>cis</i> -Cyclodecene (Å)	<i>trans</i> -Cyclodecene (Å)	
C2-C3	1.504 (1.505)	1.500 (1.477)
C3-C4	1.547 (1.544)	1.546 (1.543)
C4-C5	1.538 (1.533)	1.541 (1.541)
C5-C6	1.540 (1.538)	1.552 (1.548)
C6-C7	1.538 (1.536)	1.544 (1.539)
C7-C8	1.541 (1.539)	1.552 (1.548)
C8-C9	1.538 (1.538)	1.541 (1.541)
C9-C10	1.547 (1.544)	1.546 (1.543)
C10-C1	1.506 (1.503)	1.500 (1.497)
Average: 1.541		Average: 1.546
Average difference: 0.005 Å		
<i>cis</i> -Cycloundecene (Å)	<i>trans</i> -Cycloundecene (Å)	
C2-C3	1.506 (1.505)	1.502 (1.500)
C3-C4	1.547 (1.544)	1.546 (1.541)
C4-C5	1.538 (1.535)	1.540 (1.537)
C5-C6	1.540 (1.535)	1.541 (1.537)
C6-C7	1.537 (1.535)	1.537 (1.534)
C7-C8	1.537 (1.535)	1.537 (1.534)
C8-C9	1.541 (1.539)	1.541 (1.537)
C9-C10	1.534 (1.531)	1.540 (1.537)
C10-C11	1.544 (1.540)	1.546 (1.541)
C11-C1	1.504 (1.504)	1.502 (1.500)
Average: 1.540		Average: 1.541
Average difference: 0.001 Å		

Note: Values calculated at B3LYP and LMP2/cc-pVTZ levels (LMP2 values in parentheses). Average values calculated with B3LYP/cc-pVTZ bond lengths only.

Table 7. Calculated C=C Bond Lengths

Cycloalkene	C=C Bond Length/Å		
	AM1	B3LYP/ cc-pVTZ	LMP2/ cc-pVTZ
<i>cis</i> -Cycloheptene	1.336	1.330	1.340
<i>trans</i> -Cycloheptene	1.349	1.332	1.345
<i>cis</i> -Cyclooctene	1.334	1.331	1.342
<i>trans</i> -Cyclooctene	1.341	1.329	1.342
<i>cis</i> -Cyclononene	1.335	1.331	1.342
<i>trans</i> -Cyclononene	1.338	1.329	1.341
<i>cis</i> -Cyclodecene	1.336	1.333	1.344
<i>trans</i> -Cyclodecene	1.336	1.327	1.339
<i>cis</i> -Cycloundecene	1.336	1.332	1.343
<i>trans</i> -Cycloundecene	1.336	1.329	1.340

creases as ring size decreases, demonstrating increased ring strain in smaller rings. Only in *trans*-cycloundecene are the average bond lengths of the *trans* isomer not significantly longer than they are in its *cis* counterpart.

At the semiempirical level (AM1), the length of the C=C double bond in the *trans* isomers decreases as ring size increases (Table 7). However, at higher levels of theory two factors appear to be working in close competition, making the trends in bond length as a function of the isomer and ring size less predictable. π -bond distortion should cause a C=C bond to be slightly longer than ideal. Likewise, van der Waals strain between the eclipsing groups on the same side of the double bond also cause an increase in the length of the double bond. *Trans*-cycloheptene and *trans*-cyclooctene have the greatest π -bond distortion but the least degree of van der Waals strain as a result of pyramidalization at the sp^2 -carbon atoms. As a result, the ab initio methods predict only a slight decrease of 0.005 Å at the B3LYP/cc-pVTZ and 0.006 Å at the LMP2/cc-pVTZ level in the C=C bond length as ring size increases (from $n = 7$ to $n = 10$) and π -bond distortion becomes less pronounced.⁸ However, only in comparing *cis* versus *trans*-cycloheptene with these methods does one find that the *trans* double bond is longer than the *cis* (Table 7). Surprisingly, in spite of the π -bond distortion immediately obvious upon inspection of the molecular geometry of *trans*-cycloheptene and cyclooctene, the C=C double bond suffers only a slight increase in length in comparison to its *cis* isomer. The C-C single bonds show a much larger degree of stretching in the *trans* versus the *cis* isomers in seven- and eight-membered rings.

Conclusion

Four effects can be envisioned in *trans* cycloalkenes of medium-sized rings to allow the two ends of the double bond to be reconnected to one another when the tether is shorter than ideal:

- nonoptimal bond lengths (both shortening of some and lengthening of other bonds is needed),
- expansion or contraction of sp^3 -carbon-centered bond angles,
- twisting (torsion) about the C=C double bond, and
- pyramidalization of the sp^2 -hybridized carbons.

Prior to this investigation we expected to see increases in bond lengths and changes in bond angles about sp^3 carbons as the principal means in which medium-sized rings accommodate a trans double bond. Changes in bond length in both C–C single and C=C double bonds do occur, with the former being more pronounced than the latter. Significant bond-angle distortions about sp^3 carbons are also seen in *trans*-cycloheptene through *trans*-cyclononene. We were most surprised to find just how pronounced C=C double bond torsion and pyramidalization are in the trans cycloalkenes up to *trans*-cyclododecene. The trans cycloalkenes thus provide an excellent series of examples that clearly demonstrate the geometric suppleness of a C=C double bond.

Computational Methods

Geometry optimization calculations and frequency calculations with both semiempirical and ab initio methods were carried out using Titan (13). Titan uses localized MP2 (LMP2) procedures in which HF orbitals are localized before MP2 procedures are used. Calculations that involve solvation effects use the SM4.5 model provided in Titan. Frequency calculations were performed only at the B3LYP level.

^WSupplemental Material

Supplemental materials include Spartan (.sxf) files, Protein Data Bank (.pdb) files of the optimized geometries (for use with Chem3D), Chime images, and Cartesian coordinates, along with instructions for downloading and viewing the files (15).

Notes

1. In an article that accompanies this one (14), we compare twist angles and “p-orbital misalignment angles”. p-Orbital misalignment angles have been defined as the dihedral between π orbital axis vectors that are assumed to make equal angles to each of the σ bonds in pyramidalized alkenes. In that article we also provide details regarding the pyramidalization of sp^2 -hybridized carbon atoms that accompanies twisting about the double bond and a theoretical rationale for the strain relief that pyramidalization provides to twisted alkenes.

2. For each set of isomers, theory predicts slightly more favorable solvation effects for the cis isomer. The calculated $\Delta\Delta H$ values between the cis and trans isomers calculated using B3LYP/cc-pVTZ geometries and energies and including solvation effects appear below:

Ring Size	$\Delta\Delta H/(\text{kcal/mol})$
7	30.3
8	11.1
9	4.4
10	3.5
11	-0.53

3. On enthalpy grounds, *cis*-cyclododecene is lower in energy than trans by 0.41 kcal/mol. However, on free energy grounds, all cycloalkenes of 11 members or more show an energetic preference for the trans isomer (4a).

4. This definition was useful for us when performing the exercise described in ref 3 owing to limitations in the visualization software. Full versions of Spartan or Titan are needed to define a plane and measure angles with that plane.

5. The twisting of the exterior and interior lobes relative to one another is difficult to discern in Figure 6, but it is easily seen when looking at the images in the Supplemental Materials.^W

6. For the sake of comparison, we note that one should not expect 109.5° C–C–C bond angles. For example, the central bond angle in propane is also somewhat larger than the tetrahedral angle, at approximately 112° .

7. In a separate study (see Note 1) in which we examined the twisting and resulting pyramidalization of the C=C double bond in *trans*-2-butene we did not find that the vinylic bond shortened with increased twisting as seen in the trans cycloalkenes.

8. In the previously mentioned study using *trans*-2-butene (see Note 1) the C=C double bond length is found to increase from 1.328 Å to 1.343 Å with 90° twisting of the allylic carbon atoms.

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