Understanding Rotation about a C=C Double Bond

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Many organic textbooks *(1)* indicate that 90° twisting of a C=C double bond results in breakage of the π bond and formation of a diradical product. In other words, "for rotation to occur around a double bond, the π bond must break and re-form" *(1a)*. Perhaps it is due to pictures like Figure 1 *(1a)*, which appear with minor variations in many organic textbooks, or perhaps it is a result of working with rigid plastic or wooden model sets that our students (and maybe some organic instructors, too) believe the C=C π bond to be rigid and incapable of accommodating any flexing and twisting. However, the twisted and pyramidalized nature of the double bond in *trans*-cyclooctene has been known since 1975 *(2)*. This article focuses on the process and energetic cost of twisting around a C=C double bond. As a result of this work, and an increased familiarity with the literature published on this topic, we have made personal adjustments in our mental picture of the flexibility of C=C double bonds.

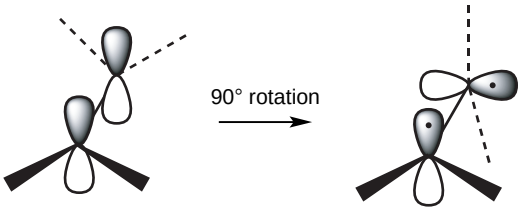


Figure 1. Textbook illustration of π-bond twisting.

Twist Angles Defined

Pyramidalization angle (Φ) is the angle between the plane defined by C2, R″, and R‴ and the line extending from the C=C double bond (Figure 2). Various researchers have used quantum mechanical calculations to determine the electronic nature of pyramidalization in several different alkenes *(3–5)*. It has been found that pyramidalization of sp^2 carbon atoms is an unanticipated consequence of bond angle distortion (Θ) and twisting (*T*) *(6, 7)* (Figure 2). Twist angle is defined here as the angle between the normals drawn to the plane containing C1, R, and R′ and the plane containing by C2, R″, and R‴. This angle is straightforward to conceptualize (Figure 2) when only rotation about the C=C double bond is considered. However, as mentioned above, twisting is accompanied by pyramidalization in the systems examined here, and so an alternative measurement of the degree the π bond is twisted (p-orbital misalignment angle, ϕ) will be used to quantify twisting. A discussion of p-orbital misalignment angle will follow.

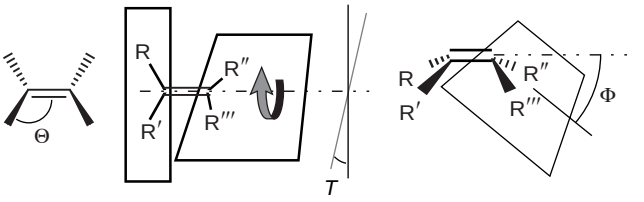


Figure 2. Angles defined (pictured from left to right): bond angle distortion (Θ), twist angle (*T*), and pyramidalization angle (Φ).

Computational Methods

Geometry optimization calculations and frequency calculations were carried out using Titan *(8)*. Both B3LYP/cc-pVTZ and LMP2/cc-pVTZ methods were used in the double bond rotation calculation of *trans*-2-butene. Multiconfigurational self-consistent field (MCSCF) calculations using two models, CAS (2,2) and (4,4), were performed with Gaussian 03 *(9)*.

Twisting and Pyramidalization in *trans*-2-Butene

The energetic requirement for twisting about a double bond in *trans*-2-butene was calculated using B3LYP, LMP2, CAS (2,2), and CAS (4,4) methods with the cc-pVTZ basis set. Results of this investigation with the various methods are illustrated in Figure 3. The dihedral angle C1−C2=C3−C4

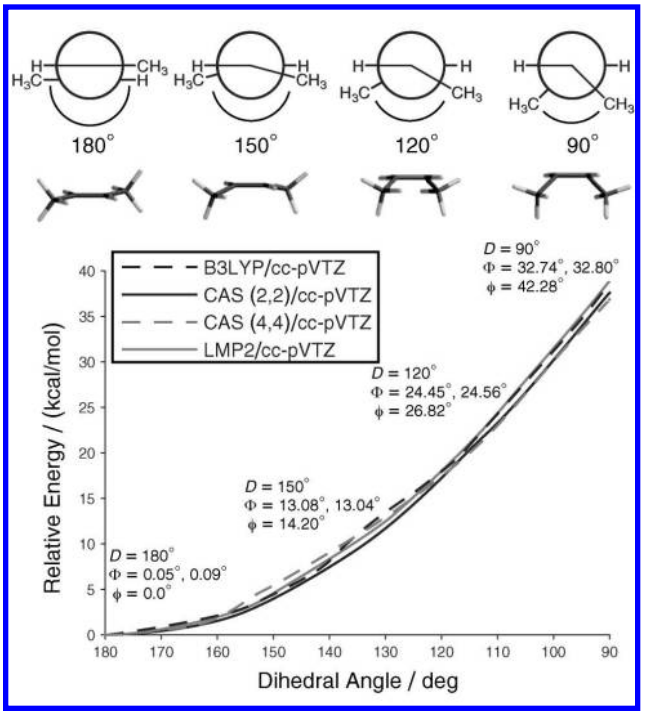


Figure 3. The energetic requirement for twisting the allylic carbon atoms toward each other in *trans*-2-butene. Pyramidalization angles (Φ) and p-orbital misalignment angles (ϕ) appear for each of the dihedral angles (*D*) pictured.

was reduced from its ideal 180° to 90° in 10° increments. The twisting of the double bond causes only minimal lengthening of the C=C bond: 1.328 Å in the ideal and fully optimized structure versus 1.343 Å in the most twisted structure with a C1−C2=C3−C4 dihedral angle of 90°. Most importantly, the energetic cost of a 90° twist (38.8 kcal/mol at the B3LYP level and 39.1 kcal/mol at the MP2 level) is much less than the strength of a C=C π bond itself. As illustrated here and examined elsewhere, decreasing the dihedral angle from 180° results in a less pronounced distortion of the π bond *if* it is accompanied by an out-of-plane bending—pyramidalization—of the sp^2 carbon atoms *(6, 7)*. The degree of pyramidalization appears in Figure 3.

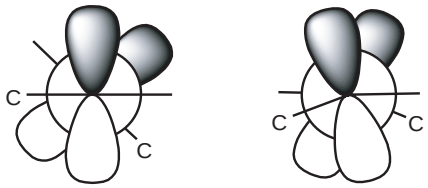


Figure 4. On the left is a Newman projection demonstrating what is referred here as pure twisting of the π bond; on the right, twisting with pyramidalization. In each case, the dihedral angle between allylic carbons is 135°. Without pyramidalization, the p-orbital misalignment angle is 45°; with pyramidalization, the angle is 18°.

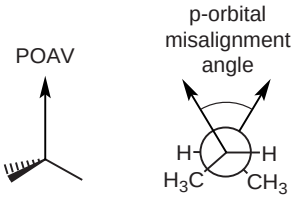


Figure 5. p-Orbital axis vector (POAV) and p-orbital misalignment defined.

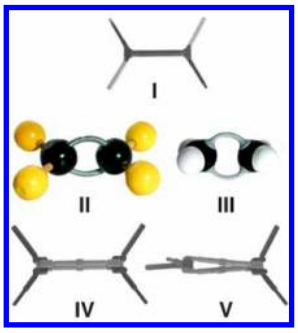


Figure 6. Models pictured to demonstrate capability of being twisted. The model types are Fieser (**I**), Sargent (**II**), Molymod (**III**), and Darling (**IV** and **V**).

Table 1. Absolute and Relative Energies of Triplet *trans*-2-Butene

Method	Absolute Energy/ hartrees	Relative Energy/ (kcal/mol)
B3LYP	-157.18451	65.7
LMP2	-156.66846	69.6
CAS (4,4)	-156.10545	65.9

As can be seen from the graph, pyramidalization increases as the double bond is progressively twisted. As a result of pyramidalization, even at very large twist angles, most of the strength of the π bond (i.e., orbital overlap) is retained. Note that in Figure 4 each of the two drawings shows a dihedral angle between the allylic carbon atoms of 135°. However, the orbital overlap in the pyramidalized structure (right) is much larger than in the unpyramidalized structure (left).

Previously, Haddon defined the p-orbital axis vector (POAV) in order to measure the direction of the p-orbital at each carbon atom in nonplanar alkenes (Figure 5). The p orbital is assumed to make equal angles to the three σ bonds in pyramidalized alkenes *(10)*. In this work, the POAV was located at each carbon atom of the double bond and then used to measure the POAV torsion angle in order to quantify the p-orbital misalignment angle (ϕ). ϕ values are included in Figure 3 for the three illustrated dihedral angles of 150°, 120°, and 90° in twisted *trans*-2-butene. These misalignment angles are slightly less than half the measured C−C=C−C dihedral angle differences from ideality. For example, at a C1−C2=C3−C4 dihedral angle of 150° without pyramidalization, ϕ should be 30°; the calculated misalignment angle, however, is only 14.2°. This retention of p-orbital overlap (and hence, π-bond strength) as a result of pyramidalization has been substantiated in earlier works *(10)*.

To test the validity of our methods we calculated the energy of the 90° twisted triplet 2-butene diradical relative to the energy of *trans*-2-butene (Table 1). This structure, illustrated in Figure 1, arguably represents the barrier to rotation about a double bond *(11)*. These values are in good agreement with experimental estimates of the π-bond strength in ethylene of approximately 65 kcal/mol *(12)*. However, ab initio molecular dynamics calculations suggest that trans–cis isomerizations of ethylene and stilbene involve structures that are not planar: they are both twisted and pyramidalized *(13)*.

The authors would like to emphasize that the preceding discussion is not new to the literature. Pyramidalization in twisted alkenes has been well documented *(3–7)*. Our purpose in writing this article is to provide instructors with a simple vehicle for rectifying the common misrepresentation of C=C double bonds as rigid and inflexible. A suitable entry point for introducing students to the idea of a flexible C=C double bond is in conjunction with discussions of cis and trans isomers of cycloalkenes *(14)*.

Models

Some model sets help to reinforce the misconception of the rigid double bond, although a few types are capable of animating twisting around a C=C double bond. Pictured at the top of Figure 6, Fieser models (**I**) allow for essentially *no* twisting of a double bond. Any significant torsion of the

C=C double bond results in not only breaking the bond, but also irreparably damaging the model. Other model sets, for example Sargent (**II**), Molymod (**III**), and Darling (**IV** and **V**), will allow more substantial twisting to occur in the double bond. Both Fieser and Darling model sets are assembled in a similar manner and both represent line–angle structural formulas of organic molecules. However, the flexibility of the Darling models is depicted explicitly in the last image (**V**), where the model has accommodated a twist of almost 90° in the C=C double bond. Models that are capable of demonstrating some twisting about the C=C double bond more closely approximate a true C=C double bond. However, theory predicts that when torsion occurs about a C=C double bond, the π bond distorts in order to maintain as much of its strength as possible. To our knowledge, no model set can possibly demonstrate the pyramidalization that results from twisting a C=C double bond, and pyramidalization is responsible for the retention of π-bond strength in twisted alkenes.

Is the *trans*-2-Butene Model Meaningful? Real-World Manifestations

Medium-sized trans cycloalkenes have twisted double bonds. For example, the twisted and pyramidalized nature of the double bond in *trans*-cyclooctene has been experimentally substantiated, and theory is in agreement with the experimental structure. Figure 7 illustrates the twisted and pyramidalized nature of the C=C double bond in the trans geometric isomer of cyclohexene, cycloheptene, cyclooctene, and cyclononene. Distortion of the π bond can be illustrated by viewing the calculated HOMO. For example, see Figure 8, which illustrates the HOMO in *trans*-cyclooctene.

As seen in the *trans*-2-butene model and in the medium-sized trans cycloalkenes, dihedral angles markedly smaller than 180° result in a twisting of one lobe of the π bond with respect to the other, an unequal distribution of electron density on either face of the double bond, and an increase in the interaction between the σ and π bonds in the HOMO. According to Fukui, this σ/π mixing causes the unsymmetrical distribution of the π electron density on both faces of the double bond, an effect that he termed "nonequivalent orbital extension" *(15)*.

To assess the validity of the model, the p-orbital misalignment angle was measured in B3LYP/cc-pVTZ optimized *trans*-cyclooctene geometry to compare with *trans*-2-butene twisted to the same dihedral angle as the C8−C1=C2−C3 dihedral angle in *trans*-cyclooctene. For these systems (depicted explicitly in Figure 8), the p-orbital misalignment angle was measured at 19.51° in *trans*-cyclooctene and 18.52° in *trans*-2-butene. Further geometric similarities become apparent in comparing the *trans*-2-butene model with the geometries of the other trans cycloalkenes. When the C−C=C−C dihedral angles in *trans*-2-butene are constrained to the same value as the C*n*−C1=C2−C3 dihedral angles found in *trans*-cyclohexene through *trans*-cyclodecene, the resultant p-orbital misalignment angles and pyramidalization angles are nearly identical in the two systems (compare the data found in Tables 2 and 3).

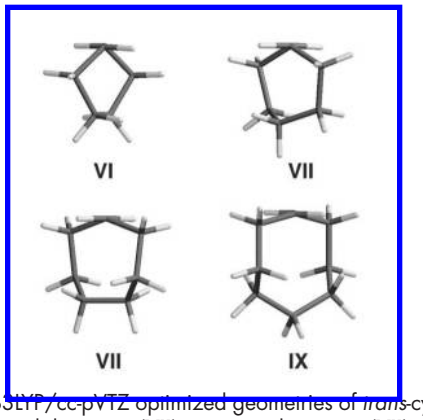


Figure 7. B3LYP/cc-pVTZ optimized geometries of *trans*-cyclohexene (**VI**), *trans*-cycloheptene (**VII**), *trans*-cyclooctene (**VII**), and *trans*-cyclononene (**IX**). The two carbons of the alkene bond are superimposed at the top of the structure.

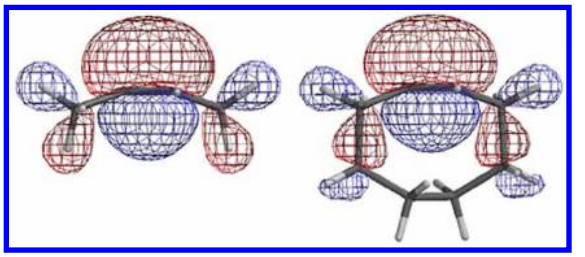


Figure 8. HOMOs of *trans*-2-butene (left) constrained to a C1−C2=C3−C4 dihedral angle of 138°, which is the same as the C8−C1=C2−C3 dihedral angle found in *trans*-cyclooctene (right).

Table 2. p-Orbital Misalignment Angles, ϕ, and Pyramidalization Angles, Φ, in Trans Cycloalkenes

Trans Cycloalkene	Calc Dihedral Angle/deg	ϕ/deg	Φ/deg
Cyclohexene	88.98	44.53	41.88, 41.98
Cycloheptene	116.29	29.71	28.14, 29.55
Cyclooctene	136.88	19.51	18.74, 18.74
Cyclononene	148.96	15.19	12.97, 12.97
Cyclodecene	167.88	7.84	5.20, 5.21

Table 3. p-Orbital Misalignment Angles, ϕ, and Pyramidalization Angles, Φ, in the Twisted 2-Butene Model

Constrained Dihedral Angle/deg	ϕ/deg	Φ/deg
88.98	38.91	32.8
116.29	29.85	25.09
136.88	18.52	17.22
148.96	15.23	12.57
167.88	5.93	5.46

Olefin Strain Energy in *trans*-Cycloalkenes

With the geometric similarity established between the twisted *trans*-2-butene model and the trans cycloalkenes, we felt that the model could be used to approximate the contribution to the strain energy caused exclusively by the trans C=C double bond in a series of trans cycloalkenes. That is, we will use the 2-butene model to isolate the strain owing to twisting alone. Then, by subtracting this from the total strain energy in cycloalkenes, we can determine the proportion of the strain that comes from twisting as opposed to other sources.

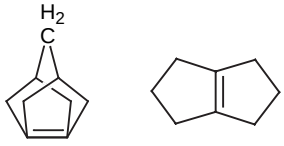
Four nonideal geometric consequences have been calculated, and in some cases measured experimentally, in the trans cycloalkene isomers of medium-sized rings. These geometric distortions are necessary to allow the two ends of the double bond to be reconnected to one another through the available $(CH_2)_n$ tether when $n < 8$:

1. Nonoptimal bond lengths (both shortening of some and lengthening of other bonds);
2. Expansion or contraction of sp^3 carbon-centered bond angles;
3. Twisting (torsion) about the C=C double bond; and
4. Pyramidalization of the sp^2 hybridized carbons.

In other words, the strain energy in trans cycloalkenes may be manifested in the aliphatic portion of the ring (effects 1 and 2 above), the C=C double bond (effects 3 and 4 above), or both.

Olefin strain energy (OSE) has been defined as the difference in strain energy between an alkene and its hydrogenated product. OSE can be obtained computationally by comparing the calculated heat of hydrogenation of an alkene with the calculated heat of hydrogenation of an unstrained reference alkene *(3, 16)*. For example, in calculating the OSE caused by the pyramidalized double bond in **X**, **XI** (Figure 9) would be used as the unstrained reference alkene. OSE is $\Delta H_{\text{hydrogenation}}(\mathbf{X}) - \Delta H_{\text{hydrogenation}}(\mathbf{XI})$. We used the cis isomer as the reference for each trans cycloalkene isomer. Thus, the calculated energy difference between the cis and trans isomers of each cycloalkene was used as part of the OSE value. The cis isomer is not exactly a perfectly matched unstrained reference because there is a difference in energy between unstrained cis and trans double bonds that needs to be taken into account. Mathematically we calculated the OSE for the trans isomers as $\Delta E_{\text{(cis-trans) cycloalkene}} - \Delta E_{\text{(cis-trans) 2-butene}}$.

We used the energy difference *cis*-2-butene and *trans*-2-butene twisted to a C−C=C−C dihedral angle that matches those found in the trans cycloalkenes as the energetic cost of the double bond in the trans cycloalkenes, $\Delta E_{\text{(cis-twist trans) 2-butene}}$. The calculated OSE and the contributions of the double bond to the strain energy in the trans cycloalkenes are listed in Table 4. From *trans*-cyclohexene through *trans*-cyclononene the majority of the strain energy is caused by twisting about the C=C double bond. The approximated strain caused by the twisted C=C double bond in the trans isomers of cyclohexene through cyclononene ranges from 64–87% of the total strain energy. There is minimal calculated twisting and pyramidalization in *trans*-cyclodecene; likewise, the calculations show a small contribution from the C=C double bond to its total OSE. It is noteworthy that medium-sized cycloalkenes place most of the strain energy in distortions to the C=C double bond, as opposed to other possible locations.



X **XI**

Figure 9. Pyramidalized double bond in **X**, and the unstrained reference alkene **XI** .

Table 4. C=C Contribution to Strain Energy

Trans Cycloalkene	OSE	$\Delta E_{\text{(cis-twist trans) 2-butene}}$ / (kcal/mol)	C=C Contribution (%)
Cyclohexene	55.3[a]	40.2	72.7
Cycloheptene	31.2[a]	20.1	64.4
Cyclooctene	12.7[a]	9.3	73.2
Cyclononene	5.5[a]	4.8	87.3
Cyclodecene	4.6[a]	0.8	17.4
Cyclohexene	53.0[b]	40.6	76.6
Cycloheptene	28.8[b]	20.3	70.5
Cyclooctene	11.7[b]	9.3	79.5
Cyclononene	4.4[b]	3.2	72.7
Cyclodecene	4.7[b]	1.0	21.3

[a]Calculated using $\Delta E_{\text{(cis-trans)}}$ 2-butene value of 1.3 kcal/mol (B3LYP/cc-pVTZ).

[b]Calculated using $\Delta E_{\text{(cis-trans)}}$ 2-butene value of 1.4 kcal/mol (LMP2/cc-pVTZ).

Conclusion

A C=C double bond is not rigid and inflexible. Significant distortions of a double bond are possible without "fatal" reduction in the strength of the π bond. This is due to the pyramidalization of sp^2 hybridized carbon atoms that accompanies twisting. Far from being an esoteric point suitable only for advanced students, this idea can easily be explained to undergraduates. When introducing the topic of alkene structure, one could reinforce the idea of a flexible double bond by using a model set that demonstrates some degree of twisting about the C=C double bond *is* possible. Then, simple reference to a diagram like Figure 4 will clearly show students the increase in p-orbital overlap that accompanies (and explains) pyramidalization in twisted alkenes. Furthermore, measurements of OSE allow us to see explicitly that the π bond is an ideal location for expressing strain. Indeed, trans cycloalkenes smaller than cyclononene probably could not exist if not for the geometric suppleness of the C=C double bond.

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