Isomerization Barriers and Strain Energies of Selected Dihydropyridines and Pyrans with Trans Double Bonds

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The stability of *cis*,*trans*-dihydropyridines and *cis*,*trans*-pyrans has been studied using ab initio methods. The strain introduced by the trans double bond has been determined relative to the *cis*,*cis*-isomers and introduces 58−69 kcal·mol^{-1} of strain energy, at the G3 level of theory, depending on the particular isomer. Double bond rotation barriers have been calculated at the MRMP2/MCSCF level and range from 2.2 kcal·mol^{-1} to 11.0 kcal·mol^{-1}, significantly lower than butadiene (50.3 kcal·mol^{-1}). Evidence of resonance through delocalization of the π electrons is present for the conjugated double bond isomers which lowers the activation barriers. The transition states for trans double bond rotation have significant biradical character but markedly less than that for butadiene. The early transition states with H−C═C−H dihedral angles of 130−150°, as opposed to 90° for butadiene, are consistent with the reduction in the natural orbital occupation numbers. We could not locate a minimum for a structure having both double bonds in the trans configuration and so report that one trans bond is the most the rings can accommodate.

Introduction

Molecular bond and ring strain have been of interest as a way to store potential energy. The quadricyclane−norbornadiene strained ring couple has been studied extensively for the possibility of storing solar energy.[1−8] The synthesis of cubane was first reported by Eaton and Cole,[9] and this highly strained structure has been the basis of high energy density uses such as explosives[10] and fuels.[11] Tricyclo[3.1.0.0^{2,6}]hexane (TC6) was first synthesized by Cristl and Bruntrup;[12] it was not immediately proposed as a high energy density candidate, but its two fused cyclopropane rings make for a highly strained but thermally stable structure. The thermal decomposition to cyclohexadiene was proposed to proceed through either a biradical intermediate or through a concerted mechanism in which 1,3-cyclohexadiene was the product. The concerted mechanism would produce the highly strained (*E*,*Z*)-1,3-cyclohexadiene as an intermediate following the Woodward−Hoffmann rules.[13] The biradical mechanism could bypass this strained intermediate directly producing cyclohexadiene. There were varied opinions about the efficacy of a pyrolysis mechanism which included the (*E*,*Z*)-1,3-cyclohexadiene intermediate, particularly whether this (and related) structure(s) could actually be a minimum on the potential energy surface.[12,14,15] We reported ab initio calculations[16] which revealed that this structure is indeed a minimum on the PES and an intermediate in the thermal decomposition of TC6 with a barrier for double bond rotation of only 2.8 kcal·mol^{-1}.

Other small cyclic hydrocarbons with a trans double bond have been reported and are also of interest for their strained geometries and possibilities as intermediates in isomerization reactions. The trans double bond in these smaller rings is strained in that the H−C═C−H dihedral angle is 180°, but the C−C═C−C dihedral angle is considerably less than 180° to enable a cyclic geometry. (*E*)-Cyclooctene is the smallest cyclic structure with a trans double bond that is stable at room temperature.[17] (*E*)-Cycloheptene is not stable at room temperature, but several studies have been reported at low temperature using techniques such as NMR, UV, and Raman spectroscopies.[18−20] The activation energy for thermal isomerization of *trans*- to *cis*-cycloheptene was measured to be 18.7 kcal·mol^{-1}.[21] Experimental isolation of the six carbon *trans*-cyclohexene has not been reported, but the activation barrier for double bond rotation has been determined using ab initio methods to be about 10 kcal·mol^{-1} (MCSCF(2,2)) and 9.1 kcal·mol^{-1} (DFT).[22,23]

As the size of the ring reduces, the activation barrier for double bond rotation decreases in harmony with the increased strain of the smaller ring. This is even more pronounced with the 1,3-cycloalkadienes: the seven-carbon (*E*,*Z*)-1,3-cycloheptadiene has a 20 kcal·mol^{-1} calculated barrier for trans double bond rotation[24] compared to 17.4 kcal·mol^{-1} for the six carbon (*E*,*Z*)-1,4-cyclohexadiene (see below) and 2.8 kcal·mol^{-1} for (*E*,*Z*)-1,3-cyclohexadiene.[16]

We were interested in the possibility of using heteroatoms or adding functional groups to the six-membered ring to raise the barrier of the double bond rotation making the trans structure more stable. This particular study looks at the addition of a nitrogen or oxygen atom in the ring and its effect on the barrier for trans double bond rotation.

Computational Methods

The strain introduced by replacement of a cis with a trans double bond in the dihydropyridine and pyran rings was expected to be substantial and of interest. Therefore, the relative strain energy was determined by comparing the energies between the structures from the cis and trans configurations for each geometric isomer. By setting the zero point at the energy of the cis isomers, the trans isomers were compared for each set, that is, for (*E*,*Z*)-2,4-dihydro-1,6-pyridine, the strain energy was determined by comparing its energy to that for (*Z*,*Z*)-2,4-dihydro-1,6-pyridine. For wave functions adequately represented by a single electronic configuration, the relative energies were determined at the G3[26] level using the Gaussian 03 suite of programs.[25] The natural orbital occupation numbers from the

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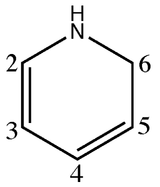

Figure 1. Numbering scheme for 1,6-dihydropyridine.

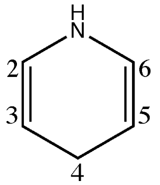

Figure 2. Numbering scheme for 1,4-dihydropyridine.

MCSCF calculations were used to measure the amount of multireference character of the wave function.

For the double bond trans → cis isomerization reactions, calculations were performed using the GAMESS[27] quantum chemistry program. Since the transition states for the double bond isomerization reactions have considerable singlet biradical character, a multiconfiguration wave function was necessary. The active space chosen consists of the σ and π occupied and virtual orbitals between all double-bonded carbon atoms comprising 8 electrons in 8 orbitals, using localized hartree-fock orbitals. Methods using both determinant CI[28] and configuration state functions[29,30] were used to perform the MCSCF calculations. Geometries and harmonic vibrational frequencies of the minima and transitions states were obtained using the 6-31G(d,p) basis set.[31] Analytic gradients were used for the geometry searches, while harmonic frequencies were determined using either finite differences of the analytic first derivatives or analytic second derivatives.

Dynamic electron correlation was included by performing single point energy calculations at the single state second-order MRMP[32] level at the MCSCF optimized geometries. A series of basis sets were used for these calculations including the 6-31G(d,p),[31] cc-pVDZ,[33] and cc-pVTZ[34] contraction schemes. For the cc-pVTZ basis set, the virtual orbitals in the MCSCF active space were constructed from the localized occupied orbitals by changing the signs of the appropriate coefficients.

The transition states for double bond rotation are fairly evident from the structures, but intrinsic reaction coordinate calculations were performed to confirm the connection of the TS to the reactant and product at the MCSCF level using the 6-31G(d,p) basis.

The numbering schemes for the double bond locations in the dihydropyridine and pyran structures are shown in Figures 1−4. We will use the following naming conventions throughout the text: (*E*,*Z*)-2,4-dihydro-1,6-pyridine has the C2═C3 double bond in the trans configuration while C4═C5 is cis, and we will abbreviate it as (N)EZ24. Conversely, (N)ZE24 would be for the C2═C3 bond being cis and the C4═C5 bond in the trans configuration. For the pyrans, (O)EZ24 would be for a C2═C3 trans bond and a C4═C5 cis bond (Figure 3). Through symmetry, the (N)EZ25 is the same as (N)ZE25 as are the (O)EZ25 and (O)ZE25 structures (Figures 2 and 4).

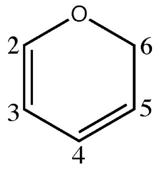

Figure 3. Numbering scheme for 2,4-pyran.

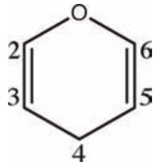

Figure 4. Numbering scheme for 2,5-pyran.

TABLE 1: Calculated Activation Barriers (kcal mol^{-1}) for Double Bond Rotation[a,b]

bond rotation	MCSCF[c]	MRMP2[d]	MRMP2[e]	MRMP2[f]
		C_5H_7N		
ZE24 → ZZ24	4.8	3.5	3.0	4.1
EZ24 → ZZ24	4.0	3.6	3.5	4.1
EZ25 → ZZ25	9.8	10.1	10.2	11.0
		C_5H_7O		
ZE24 → ZZ24	1.5	1.5	1.6	2.2
EZ24 → ZZ24	4.3	4.0	4.0	5.0
EZ25 → ZZ25	6.7	8.1	9.1	10.0
		C_6H_8		
EZ13 → ZZ13	5.1	2.6	2.3	3.1
EZ14 → ZZ14	14.7	16.2	16.2	17.4
C_2H_4 (ethene)	64.9	60.2	59.0	59.9
C_4H_6 (butadiene)	58.2	50.1	49.5	50.3

[a] Including zero-point energy correction. [b] All geometries optimized at the MCSCF/6-31G(d,p) level. [c] 6-31G(d,p) basis set. [d] MRMP2/6-31G(d,p)//MCSCF/6-31G(d,p) level. [e] MRMP2/cc-pVDZ//MCSCF/6-31G(d,p) level. [f] MRMP2/cc-pVTZ//MCSCF/6-31G(d,p) level.

Results and Discussion

The trans → cis isomerization of a double bond can occur through simple bond rotation. The activation barriers of double bond rotation for the various dihydropyridines and pyrans are listed in Table 1, along with some hydrocarbons for comparison. One of the most apparent results is the marked decrease in the trans → cis activation barrier for the ring systems compared with ethene and butadiene. Ethene has a barrier of 60 kcal·mol^{-1} for rotation of the double bond, while butadiene has a barrier of 50 kcal·mol^{-1}; the pyrans and dihydropyridines have barriers between 2 and 11 kcal·mol^{-1}. This difference can be attributed to the bond strain present in the cyclic dienes as discussed below.

The relative energies are given in Table 2; the zero reference for each set is the *cis*,*cis*-diene. For the dihydropyridines, introducing one trans bond in the ring raises the energy up to 64 kcal·mol^{-1}. Since the only difference is the cis or trans orientation of the double bond, the relative energy gives a measure of the bond strain introduced to the structure due to the trans double bond. In each case, having the trans bond adjacent to the heteroatom raises the strain energy. For the dihydropyridines, the bond strain is 64.2 kcal·mol^{-1} for (N)EZ24, while the (N)ZE24 conformer is 58.2 kcal·mol^{-1} above the zero point. There is slightly more strain in the pyrans with the (O)EZ24 structure being 68.5 kcal·mol^{-1} higher than the all cis structure, while the (O)ZE24 isomer is 58.1 kcal·mol^{-1} higher. One reason for the increase in strain energy for the trans bond adjacent to the heteroatom could be the presence of nonbonding electrons on the heteroatom. The C—N—C and C—O—C bonds are not as flexible as a C—C—C moiety because of the extra space taken up by the lone pair

TABLE 2: Relative Energies (kcal·mol^{-1}) (Including ZPE Correction)

molecule	Δ*E*(MP2)[a]	Δ*E*(MRMP2)[b]	Δ*E*(G3)
	C_5H_7N		
ZZ24	0.0	0.0	0.0
ZE24	59.2	56.6	58.2
EZ24	66.0	61.3	64.2
ZZ25	0.0	0.0	0.0
EZ25	59.0	55.0	57.8
	C_5H_7O		
ZZ24	0.0	0.0	0.0
ZE24	59.0	56.6	58.1
EZ24	71.4	65.9	68.5
ZZ25	0.0	0.0	0.0
EZ25	64.2	59.0	62.1

[a] MP2/6-31G(d,p)//MP2/6-31G(d,p) level. [b] MRMP2/cc-pVTZ//MCSCF/6-31G(d,p) level.

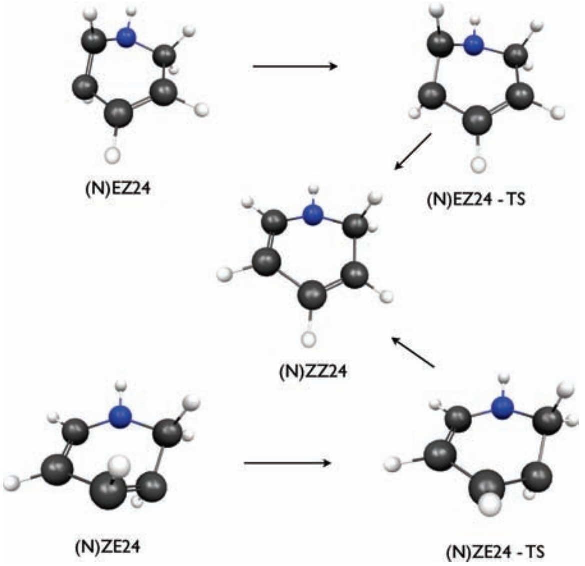

Figure 5. (N)EZ24 and (N)ZE24 trans double bond rotation with transition states (TS).

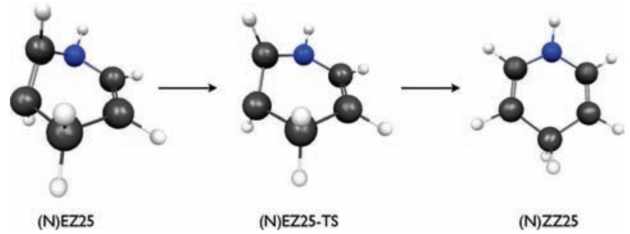

Figure 6. (N)EZ25 trans double bond rotation with transition state (TS).

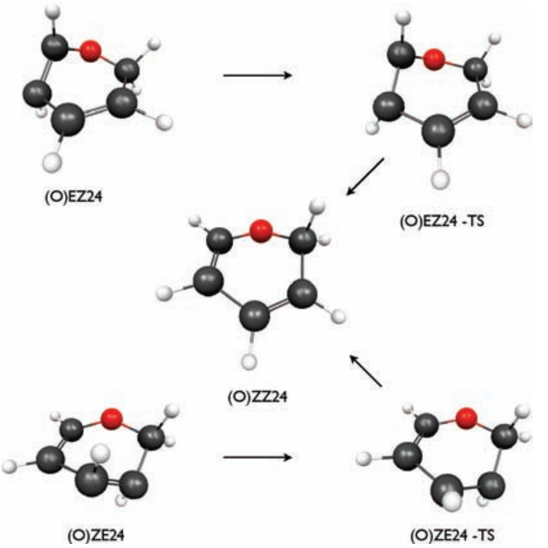

Figure 7. (O)EZ24 and (O)ZE24 trans double bond rotation with transition state (TS).

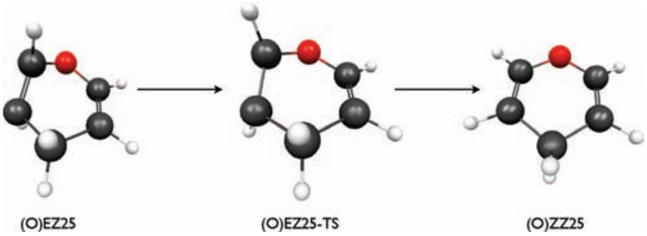

Figure 8. (O)EZ25 trans double bond rotation with transition state (TS).

electrons. The higher relative energy for (O)EZ24, compared to (N)EZ24, is consistent with two lone pairs around the oxygen atom.

The activation barriers for the dihydropyridines range from 4.1 to a high of only 11.0 kcal·mol^{-1}. The pyrans have even a lower barrier for trans double bond rotation, ranging from 2.2 to 10.0 kcal·mol^{-1}. The structures, including transition states, are shown in Figures 5−8 below.

For those structures with conjugated double bonds, we were interested in possible delocalization effects. The barriers for the ring systems with adjacent (conjugated) double bonds are much lower in each case. For the dihydropyridines, the (N)EZ25 goes to 11.0 kcal·mol^{-1} from the 4.1 kcal·mol^{-1} for the (N)ZE24 isomer, while for the pyrans the (O)EZ25 structure is 10.0 compared to 2.2 kcal·mol^{-1} for the (O)ZE24 isomer. Butadiene has similar conjugated double bonds, and its barrier for rotation is 50.3 kcal·mol^{-1}, substantially less than the 59.9 kcal·mol^{-1} for ethene. One explanation is electron delocalization in the transition state between the single electron adjacent to the cis double bond. In ethene, the H−C−C−H dihedral goes from 180° to 90.2° in the transition state making the p orbitals virtually orthogonal. The natural orbital occupation numbers for the orbitals making up the broken π bond are 1.001 and 0.9990, showing that the TS in ethene π bond rotation is essentially a pure singlet biradical. In butadiene, there are two double bonds, so electron delocalization through the p orbitals is possible. In the TS, the H1−C1−C2−H3 dihedral for the broken π bond is 95°, with NOON's for the two orbitals comprising the broken π bond being 1.000 and 1.000 also making this a pure singlet biradical. However, the p orbital on C2 is still parallel with the C3═C4 π bond, as measured by the H3−C2−C3−H4 dihedral of 180°, through which delocalization of the single electron is possible, lowering the TS energy relative to ethene.

A similar effect is possible for the ZE24 and EZ24 isomers for both dihydropyridines and pyrans; the NOONs show that the TS has significant biradical character (Table 3), although it is less than the pure biradical for the TS in ethene and butadiene. The dihydropyridine (N)ZE24 isomer has NOON values of 1.283 and 0.7163 for the orbitals making up the broken C4═C5 π bond in the TS; the H−C4═C5−H dihedral is 138.3° in the TS, substantially more than the 90° for ethene and butadiene. This is mostly due to the constraint the ring imparts upon the geometry. The H−C3−C4−H dihedral is −48.6° in the TS, reducing the overlap of the p-orbitals on C3 and C4 compared to 11° in the (N)ZZ24 isomer, but still allowing for partial

TABLE 3: Natural Orbital Occupation Numbers (NOON) for Active Space Orbitals

orbital	19	20	21	22	23	24	25	26
			C_5H_6O					
(O)EZ25	1.9819	1.9811	1.9251	1.7695	0.2302	0.0745	0.0193	0.0184
(O)EZ25 → (O)ZZ25 TS	1.9820	1.9785	1.9284	1.1215	0.8785	0.0712	0.0216	0.0183
ZZ25	1.9824	1.9822	1.9274	1.9299	0.0184	0.0177	0.0774	0.0647
(O)EZ24	1.9271	1.9808	1.9816	1.7810	0.2194	0.0184	0.0720	0.0197
(O)EZ24 → (O)ZZ24 TS	1.9252	1.9817	1.9783	1.2794	0.7204	0.0183	0.0750	0.0217
ZE24	1.9817	1.9807	1.9208	1.7549	0.2455	0.0783	0.0198	0.0184
(O)ZE24 → (O)ZZ24 TS	1.9818	1.9789	1.9199	1.3496	0.6509	0.0794	0.0213	0.0182
(O)ZZ24	1.9827	1.9819	1.9389	1.9076	0.0936	0.0593	0.0187	0.0172
			C_5H_7N					
(N)EZ25	1.9818	1.9255	1.9812	1.7955	0.2043	0.0185	0.0191	0.0741
(N)EZ25 → (N)ZZ25 TS	1.9782	1.9292	1.9821	1.1086	0.8918	0.0218	0.0182	0.0701
(N)ZZ25	1.9284	1.9823	1.9302	1.9822	0.0184	0.0774	0.0634	0.0177
(N)EZ24	1.9808	1.9209	1.9817	1.7818	0.2186	0.0197	0.0782	0.0183
(N)EZ24 → (N)ZZ24 TS	1.9781	1.9181	1.9817	1.2916	0.7090	0.0220	0.1814	0.0182
(N)ZE24	1.9287	1.9816	1.9809	1.7869	0.0183	0.2133	0.0701	0.0196
(N)ZE24 → (N)ZZ24 TS	1.9249	1.9783	1.9816	1.2830	0.0183	0.7163	0.0757	0.0218
(N)ZZ24	1.9819	1.9087	1.9826	1.9401	0.0187	0.0922	0.0585	0.0273

TABLE 4: Bond Lengths (Å), Angles, and Dihedrals (deg) for C_5H_7N

parameter	(N)EZ24	$TS_{(N)EZ24 \rightarrow (N)ZZ24}$	(N)ZE24	$TS_{(N)ZE24 \rightarrow (N)ZZ24}$	(N)ZZ24
N—C2	1.405	1.414	1.412	1.405	1.398
C2=C3	1.413	1.499	1.377	1.378	1.361
C3—C4	1.485	1.453	1.479	1.450	1.469
C4=C5	1.373	1.373	1.412	1.501	1.360
C5—C6	1.533	1.513	1.496	1.501	1.511
C6—N	1.496	1.473	1.493	1.473	1.454
N—C2=C3	110.3	110.3	125.8	124.9	121.4
C2=C3—C4	107.1	111.2	109.4	117.4	118.1
C3—C4=C5	109.1	116.8	107.8	110.6	119.6
C4=C5—C6	124.5	123.9	110.7	111.8	120.2
C5—C6—N	115.0	113.0	100.4	104.7	110.1
H—C2=C3	118.4	116.8	121.1	120.9	122.4
H—C3=C2	114.6	119.4	121.5	119.2	120.7
H—C4=C5	122.5	120.4	117.8	121.3	120.7
H—C5=C4	120.7	120.2	114.2	114.2	121.4
N—C2=C3—C4	83.1	61.5	9.5	2.234	0.5
N—C6—C5=C4	10.8	−3.8	−64.5	−63.9	−30.1
C2=C3—C4=C5	−45.3	−25.7	−44.4	−24.7	12.3
C6—C5=C4—C3	124.5	−1.3	78.7	57.8	3.9
H—C2=C3—H	175.7	138.5	−1.3	−3.8	−1.2
H—C3—C4—H	−87.9	−53.7	−78.2	−48.6	11.1
H—C4=C5—H	−0.6	−4.2	178.2	138.3	−1.5

electron delocalization of the single electron on C4 through the C2=C3 π bond. The (N)EZ24 isomer has a H—C2=C3—H dihedral of 138.5° for the rotation about the C2=C3 double bond, in the TS, and the value of the H—C3—C4—H dihedral is −53.7° allowing for partial electron delocalization. Both isomers have the same barrier of 4.1 kcal·mol^{-1}. Structural parameters are given in Tables 4−7.

For the pyrans, the (O)ZE24 isomer has a barrier of only 2.2 kcal·mol^{-1}, while the (O)EZ24 isomer has a barrier of 5.0 kcal·mol^{-1}. The H—C=C—H dihedral angles around the rotating trans double bond for each TS are 140.5° for the (O)ZE24 isomer and 151.5° for (O)EZ24. So, the trans double bond rotates 40° for the (O)ZE24 isomer compared to only 29° for the (O)EZ24 isomer, making the latter TS much earlier on the PES. This normally corresponds to a lower activation barrier, but with the large amount of strain released during the reaction, this factor could be more important in determining the barriers. As for possible electron delocalization, the H—C3—C4—H dihedral angles are 52° for the (O)ZE24 isomer and 61° for the (O)EZ24 isomer, showing that partial delocalization is present. Both sets of EZ24, ZE24 isomers have lower barriers than their EZ25 counterparts supporting the delocalization of an electron from the rotating π bond with the adjacent double bond in the transition state.

TABLE 5: Bond Lengths (Å), Angles, and Dihedrals (deg) for C_5H_7N

parameter	(N)EZ25	$TS_{(N)EZ25 \rightarrow (N)ZZ25}$	(N)ZZ25
N—C2	1.416	1.407	1.402
C2=C3	1.402	1.507	1.355
C3—C4	1.507	1.508	1.509
C4—C5	1.546	1.520	1.509
C5=C6	1.371	1.359	1.355
C6—N	1.441	1.411	1.402
N—C2=C3	108.773	111.819	123.235
C2=C3—C4	109.882	113.742	122.591
C3—C4—C5	99.309	107.681	110.514
C4—C5=C6	123.187	121.955	122.591
C5=C6—N	124.379	123.867	123.2325
H—C2=C3	188.880	119.967	121.648
H—C3=C2	113.077	116.259	118.604
N—C2=C3—C4	86.588	59.049	1.737
N—C6=C5—C4	0.903	0.254	−1.737
C2=C3—C4—C5	−55.449	−45.672	6.476
C6=C5—C4—C3	16.013	17.526	−6.476
H—C2=C3—H	−176.886	133.968	0.483
H—C5=C6—H	−1.347	0.392	−0.483

TABLE 6: Bond Lengths (Å), Angles, and Dihedrals (deg) for C_5H_6O

parameter	(O)EZ24	TS$_{\text{(O)EZ24} \rightarrow \text{(O)ZZ24}}$	(O)ZE24	TS$_{\text{(O)ZE24} \rightarrow \text{(O)ZZ24}}$	(O)ZZ24
O—C2	1.365	1.371	1.364	1.357	1.356
C2═C3	1.414	1.488	1.373	1.372	1.357
C3—C4	1.487	1.463	1.479	1.455	1.469
C4═C5	1.373	1.372	1.414	1.499	1.358
C5—C6	1.535	1.518	1.489	1.497	1.508
C6—O	1.441	1.421	1.457	1.433	1.412
O—C2═C3	113.6	111.9	126.5	125.7	122.6
C2═C3—C4	105.5	108.8	108.9	117.2	118.1
C3—C4═C5	108.4	114.9	107.9	109.5	118.3
C4═C5—C6	124.3	123.7	109.1	110.6	118.9
C5—C6—O	116.1	114.4	103.3	107.2	112.5
H—C2═C3	120.2	117.5	123.1	122.9	124.5
H—C3═C2	114.4	119.0	121.3	118.9	120.2
H—C4═C5	122.9	121.1	117.5	120.8	121.6
H—C5═C4	121.3	120.8	114.6	114.8	122.3
O—C2═C3—C4	83.1	66.5	5.9	0.0	−1.1
O—C6—C5═C4	11.9	−1.0	−61.1	−62.3	−30.4
C2═C3—C4═C5	−43.9	−28.8	−45.2	−25.3	13.0
C6—C5═C4—C3	4.0	−0.2	77.6	57.1	3.6
H—C2═C3—H	176.5	151.3	−1.9	−4.4	−2.3
H—C3—C4—H	88.0	60.8	79.5	51.9	12.9
H—C4═C5—H	−0.8	−3.7	178.2	140.5	−1.2

TABLE 7: Bond Lengths (Å), Angles, and Dihedrals (deg) for C_5H_6O

parameter	(O)EZ25	TS$_{\text{(O)EZ25} \rightarrow \text{(O)ZZ25}}$	(O)ZZ25
O—C2	1.391	1.369	1.362
C2═C3	1.370	1.355	1.351
C3—C4	1.544	1.519	1.506
C4—C5	1.511	1.507	1.506
C5═C6	1.402	1.502	1.351
C6—O	1.380	1.375	1.362
O—C2═C3	125.4	125.0	124.6
C2═C3—C4	123.3	122.2	122.4
C3—C4—C5	98.4	106.4	109.3
C4—C5═C6	108.0	112.1	122.4
C5═C6—O	112.1	113.6	124.6
H—C2═C3	122.8	123.4	123.8
H—C3═C2	116.7	118.0	118.0
H—C5═C6	112.8	116.7	118.0
H—C6═C5	121.1	120.9	123.8
O—C2═C3—C4	−3.1	−3.2	−0.1
O—C6═C5—C4	−86.4	−61.5	−0.1
C2═C3—C4—C5	−17.1	−15.8	0.0
C6═C5—C4—C3	54.7	44.8	0.0
H—C2═C3—H	1.0	−1.2	0.0
H—C6═C5—H	176.1	−140.9	0.0

One manifestation of strain, due to the trans double bond, appears in the dihedral angles. Although the H—C═C—H dihedral angles across the trans double bond are very close to 180° for each trans isomer, those encompassing the heavy atoms of the trans double bond are far from 180°. For example, the (N)EZ25 dihydropyridine isomer has a H—C2═C3—H dihedral of −177°, while the N—C2═C3—C4 dihedral is only 87°, about half of what would occur in a normal trans double bond. This small value for the dihedral angles for the heavy atoms is necessary to join the atoms into a ring but imparts a large amount of bond strain to the structure. The dihedral angle for the heavy atoms about the trans double bond for (N)ZE24, at 79°, is slightly smaller than that for the (N)EZ24 isomer with a value of 83°. This is also mirrored for the pyrans in that (O)ZE24 has a heavy atom dihedral angle of 78° compared to 83° for (O)EZ24. The activation barrier for the (O)ZE24 is lower, at 2.2 kcal·mol^{-1}, than for (O)EZ24, at 5.0 kcal·mol^{-1}. However, with the strain release concomitant with cleavage of the π bond, and all the associated geometric changes, it is difficult to attribute the lower barrier to just the lower dihedral angle alone: the barriers for the (N)ZE24 and (N)EZ24 are the same, even though the heavy atom dihedral angles are also slightly different.

Another manifestation of the strain is the value of the dihedral angles in the transition states, which are very early on the PES. For the (N)EZ25 isomer, the H—C3═C4—H dihedral goes from −176° to 134° in the TS, a reduction of only 52°, compared to the approximately 90° for ethylene and butadiene. The N—C1═C2—C3 dihedral likewise reduces only from 87 to 59° in the TS. The position of the trans double bond, in the ring, relative to the N or O atom did not change the transition state much; comparing the (N)EZ24 and (N)ZE24 dihydropyridine isomers, the dihedral angles about the trans double bond in the transition states are 139° and 138°, respectively. In the minimum structures they are 176° for the H—C2═C3—H dihedral in (N)EZ24 and 178° for H—C4═C5—H in (N)ZE24. Likewise the N—C2═C3—C4 dihedral in (N)EZ24 reduces from 83° to 62° in the TS, while the C3—C4═C5—C6 dihedral changes from 79° to 58° in the (N)ZE24 isomer.

One small trend that can be observed from the data in Tables 4−7 is that the heavy atom dihedral angles in the ZE24 isomers are less in the trans structure and the transition states compared to the EZ24 isomers for both the dihydropyridines and pyrans. For the pyrans, the ZE24 isomer has a C3—C4═C5—C6 dihedral of 78° while the EZ24 isomer has a value of 83°. The respective transition states for bond rotation have values of 57° and 67° for the same dihedral angles. The structural difference is that in the EZ24 isomers, the dihedral about the trans bond includes the heteroatom, while in the ZE24 isomers it does not. One explanation could be that the lone pair electrons on the heteroatom make the ring more rigid around the N or O atom, reducing the pucker associated with the trans double bond.

The C—C bond length of the trans double bond is longer than a normal double bond for each structure. Again, although the H—C═C—H dihedral angles are close to 180°, the heavy atom dihedral angles are closer to 90° in the rings, causing the p orbitals to be somewhat misaligned compared to the cis double bonds. For the dihydropyridines, the (N)EZ24 and (N)ZE24 lengths are virtually identical with C1=C2 being 1.413 Å and C3=C4 being 1.412 Å, respectively, while the cis bonds have values of C3=C4 of 1.373 Å and C1=C2 of 1.377 Å, respectively. The double bond lengths in the (N)EZ25 isomer are 1.402 and 1.371 Å, respectively. We believe the longer trans double bond lengths in the conjugated isomers is due to the larger C—C single bond lengths in the unconjugated (N)EZ25 isomer, compared to (N)EZ24 and (N)ZE24, reducing the double bond lengths in the cyclic structure.

An interesting result is the short N—C2 bond length in each dihydropyridine isomer compared to the N—C6 length. It is most different for (N)EZ24 with a 1.405 Å N—C2 length and a 1.496 Å N—C6 length. The (N)ZE24 isomer has values of 1.412 and 1.473 Å, respectively. A simple explanation would be conjugation between the lone pair on N and the adjacent double bond.

The disparity in the (N)EZ25 N—C bonds is interesting; the one adjacent to the trans double bond has a value of 1.416 Å, while the one adjacent to the cis double bond is 1.441 Å in length: in the (N)ZZ25 isomer both N—C bonds are 1.402 Å. It is possible that the lone pair on nitrogen overlaps the distorted trans π bond more so than the π bond from the cis double bond.

There are a couple of notable differences in the pyran isomers. The O—C2 bond in (O)EZ25 is slightly longer than the O—C6 bond, with values of 1.391 and 1.380 Å, respectively, opposite that of the (N)EZ25 dihydropyrindine analogue. However, in the (O)EZ24 and (O)ZE24 isomers, the O—C2 bonds are shorter than the O—C6 bonds, but the O—C2 bonds in both isomers are virtually the same in this case. It is possible that the resonance between the nonbonding O electrons and the cis double bond is greater than for the trans double bond, opposite that seen in (N)EZ25. Results for the pyrans are very similar with both the (O)EZ24 and the (O)ZE24 having a C=C bond length of 1.414 Å for the trans double bond.

Summary and Conclusions

The six membered heterocyclic rings, (*E*,*Z*)-2,4-1,6-dihydropyridine, (*E*,*Z*)-2,5-1,4-dihydropyridine, along with the pyran analogues, have been shown to be minima on the potential energy surfaces. The presence of a trans double bond adds a substantial amount of strain to the ring which is released during the isomerization process, through double bond rotation. The natural orbital occupation numbers for the π and π^* orbitals making up the trans double bonds reflect some biradical character, being approximately 1.75 and 0.25, respectively. At the transition states, the NOONs for the two orbitals comprising the breaking trans double bonds drop much closer to unity, illustrating the singlet biradical nature of the wave functions and the necessary MCSCF methods. The double bond rotation barriers of the trans double bond are very small, between 2 $\text{kcal}\cdot\text{mol}^{-1}$ and 11 $\text{kcal}\cdot\text{mol}^{-1}$, compared to 50 $\text{kcal}\cdot\text{mol}^{-1}$ for butadiene and 60 $\text{kcal}\cdot\text{mol}^{-1}$ for ethene.

The trend for the double bond rotation barriers in which those for conjugated double bonds are lowest, for each isomer studied, has been explained using electron delocalization effects.

The strain imposed by the trans double bond is greatest for the EZ24 isomer for both heteroatom rings with the trans double bond adjacent to the heteroatom which could be due to greater rigidity of the ring due to the lone pair electrons on the N or O atoms. The strain is raised by 10% between the (N)EZ24 and the (N)ZE24 isomers and 18% between the (O)EZ24 and the (O)ZE24 isomers. It is possible that the two lone pairs of electrons on oxygen makes the ring more rigid than the single lone pair on nitrogen.

We attempted to locate minima for isomers containing two trans double bonds either at the 2,4 or 2,5 positions, but none of the possibilities were located, so we conclude that the dihydropyridine and pyran rings containing two trans bonds are not stable.

The addition of an O or N atom in the ring lowered the double bond rotation barrier of the EZ25 isomers relative to (*E*,*Z*)-1,4-cyclohexadiene, by a considerable amount. Currently, we are looking at possible constituents that will raise the trans double bond rotation barrier to allow stabilization for experimental isolation and characterization.

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Supporting Information Available: Cartesian coordinates for each structure optimizaed at the MCSCF(8,8)/6-31G(d,p) level. This material is available free of charge via the Internet at http://pubs.acs.org.

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