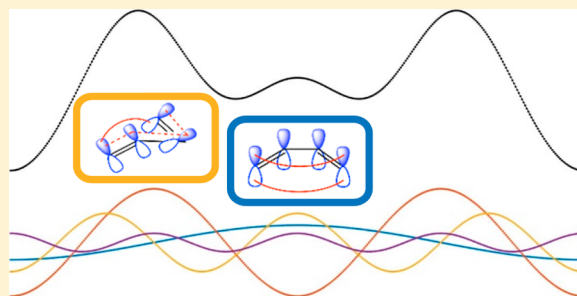


Butadiene and Heterodienes Revisited

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Supporting Information

ABSTRACT: Surprising features in a recently published high-level calculation of the rotational profile of butadiene led us to compare butadiene with a set of 17 heterodienes. The rotational profiles for this large group of compounds varied widely, thereby possessing a high information content. These data were subjected to a Fourier analysis yielding 1- through 6-fold terms: the one-fold terms represent the change in steric energy on going from 180° to 0°, while the changes in the 2-fold terms correspond to the expected change in π -delocalization energy with structure; the 3-fold terms were significant and found to be linearly correlated to the average of the atomic charges of the atoms at the central single bond of the *cis*-forms, but their origins are still not clear; we propose a novel 1,4 π -interactions that may account for this phenomenon. The 4-fold terms were at times comparable in magnitude to the 3-fold terms but overall appeared to mainly modify the 3-fold terms slightly without introducing any qualitatively new features. The 5- and 6-fold terms were negligible.



INTRODUCTION

The publication of a very high-level calculation for the butadiene torsional potential¹ renewed our interest in this compound.² It provided detailed information about the relationship between the *gauche* and *cis* forms as well as the predictions necessary to locate the weak microwave signals from the *gauche* form; an analysis of the ensuing experimental data led to detailed structural information about the *gauche* form.¹ A more global characterization of the butadiene torsional potential had been conducted previously by Boopalachandran et al.³ on the basis of analysis of Raman spectra.

Several unexpected features appeared in these results. We were particularly interested in the location of the *trans* to *gauche* transition state at a torsion angle of 101.7°, whereas one might have expected it to be at 90° where the two double bonds would be uncoupled. In addition, the transition-state energy is 6.2 kcal/mol, whereas the conjugation energy is thought to be about 4 kcal/mol based on Kistiakowsky's experimental energies of hydrogenation for 1-butene and butadiene.⁴ Finally, we were also interested in the apparent steric interactions, such as repulsion between the *endo* hydrogens that lead the *cis* form to have a higher energy than the *gauche* as well as other geometric distortions, i.e., a C–C–C bond angle that is 2° larger in the *cis* form than in *trans*.

BUTADIENE AND THE APPARENT ABSENCE OF REPULSIVE INTERACTIONS

To facilitate calculations for butadiene and other related compounds, we used the relatively inexpensive method MP2/aug-cc-pVTZ. It was found that these calculations led to a rotational potential energy curve that fairly well reproduced the higher level

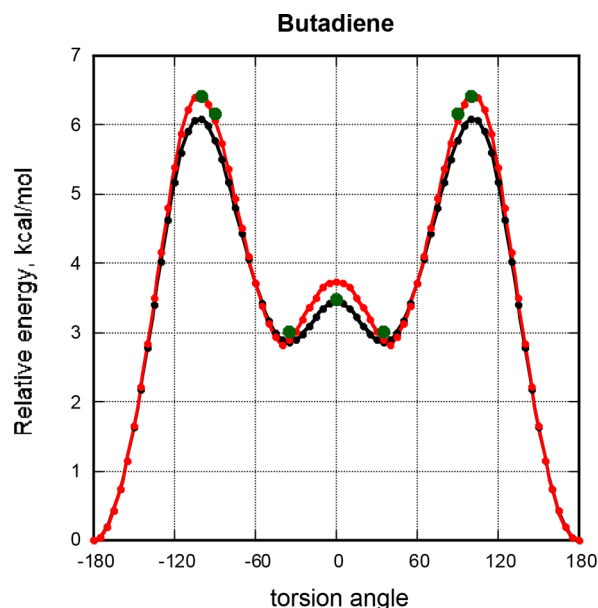


Figure 1. Optimized relative energy of butadiene as a function of the torsion angle. The MP2/aug-cc-pVTZ results are shown in red, and the higher level CCSD(T)/ANO1 results of ref 1 are in black. The green dots give the high level results of Feller and Craig.⁵

work (CCSD(T)/ANO1) (Figure 1). With this in hand, we examined the *endo* H···H nonbonded distances for the *gauche*

Received: April 28, 2018

Published: June 4, 2018



and *cis* forms. The former was 2.532 Å, while the latter was 2.254 Å; both of these distances appeared to be longer than might be expected for a repulsive interaction.

To obtain an estimate of the H...H repulsion energies at the same theoretical level as used for Figure 1, the relative energies were calculated for a pair of ethylene molecules in a plane and approaching each other sideways. The energy as a function of the H...H distance for a single pair of hydrogens is shown in Figure 2.

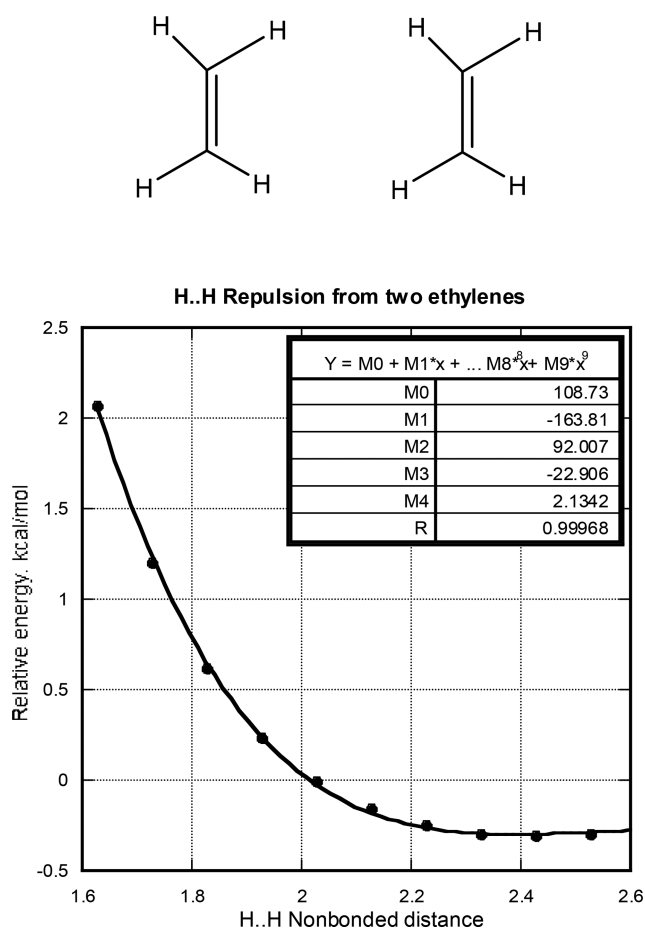


Figure 2. H...H nonbonded interaction between a pair of hydrogens.

Figure 2 shows that the repulsion energy is minimal at the H...H distance actually calculated for *cis*-butadiene. If what appears to be a repulsive interaction between the terminal methylene groups is not due to the hydrogens, what may be its source? It seemed desirable to have an estimate of the magnitude of the possible repulsive interaction. If we take the butadiene potential shown in Figure 1 and extend the curves going toward the 0° torsion angle (i.e., without a repulsive interaction) it would appear that at a minimum it would go to ~2 kcal/mol (red curve in Figure 3). Further, there is no reason to think that the delocalization energy is much different for a *cis* arrangement of the double bonds than found with the *trans* arrangement (blue curve). As can be seen in Figure 3, this leads to an estimated minimum steric energy of 1.7 kcal/mol, but it could be as large as 3.7 kcal/mol.

It is difficult to see how a simple repulsive effect could lead to such large energies at the H...H distances actually calculated for *cis*-butadiene. Therefore, we have returned to studying a group of related compounds² in hopes of gaining further information. The new data for butadiene showed that the level used in our earlier work was inadequate, and then the torsional potentials for the

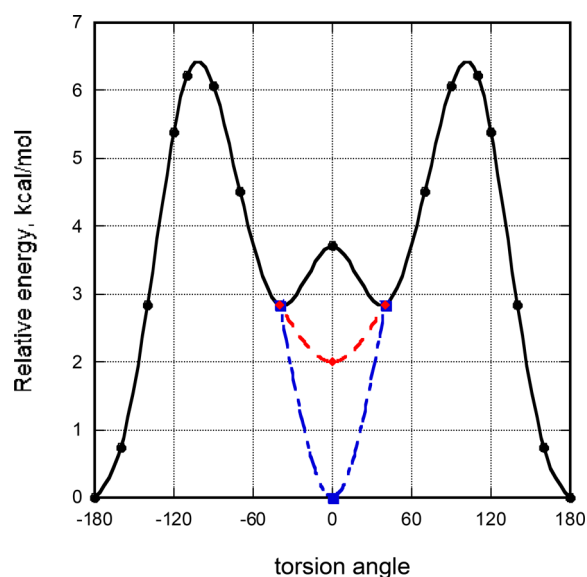


Figure 3. Possible potential curves near 0° for "butadiene" without a repulsive interaction.

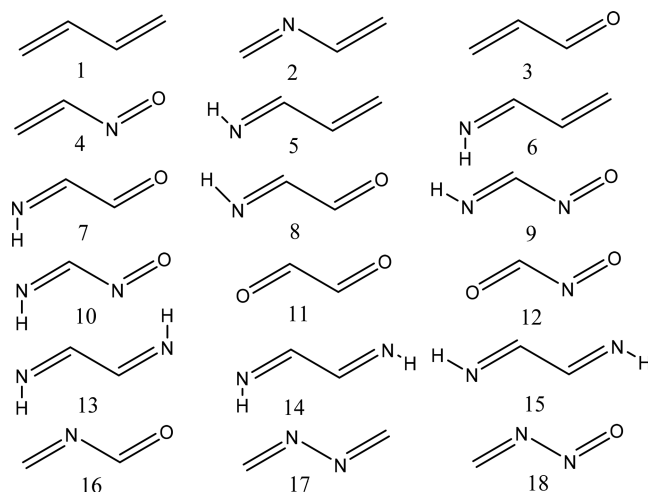


Figure 4. Structures of the compounds.

compounds shown in Figure 4 were calculated with the MP2/aug-cc-pVTZ that was found to be satisfactory for butadiene.

TORSIONAL POTENTIALS AND FOURIER ANALYSIS

The torsional potential functions that were obtained are summarized in Figure 5. (Larger copies as well as numerical values may be found in the Supporting Information.) There is a remarkably wide range of different torsional potentials and it is clear that it is necessary to find a way to allow comparisons among these compounds; the considerable variety among the rotational profiles also indicated that they have a relatively high information content. Therefore, we fit them to a six-parameter equation of the form

$$V = A_0/2 + \sum_{n=1}^6 \cos n\phi$$

The values of the first four terms from the MP2/aug-cc-pVTZ calculations are given in Table 1, as the 5- and 6-fold terms were negligible. The full set of these terms may be found in the Supporting Information.

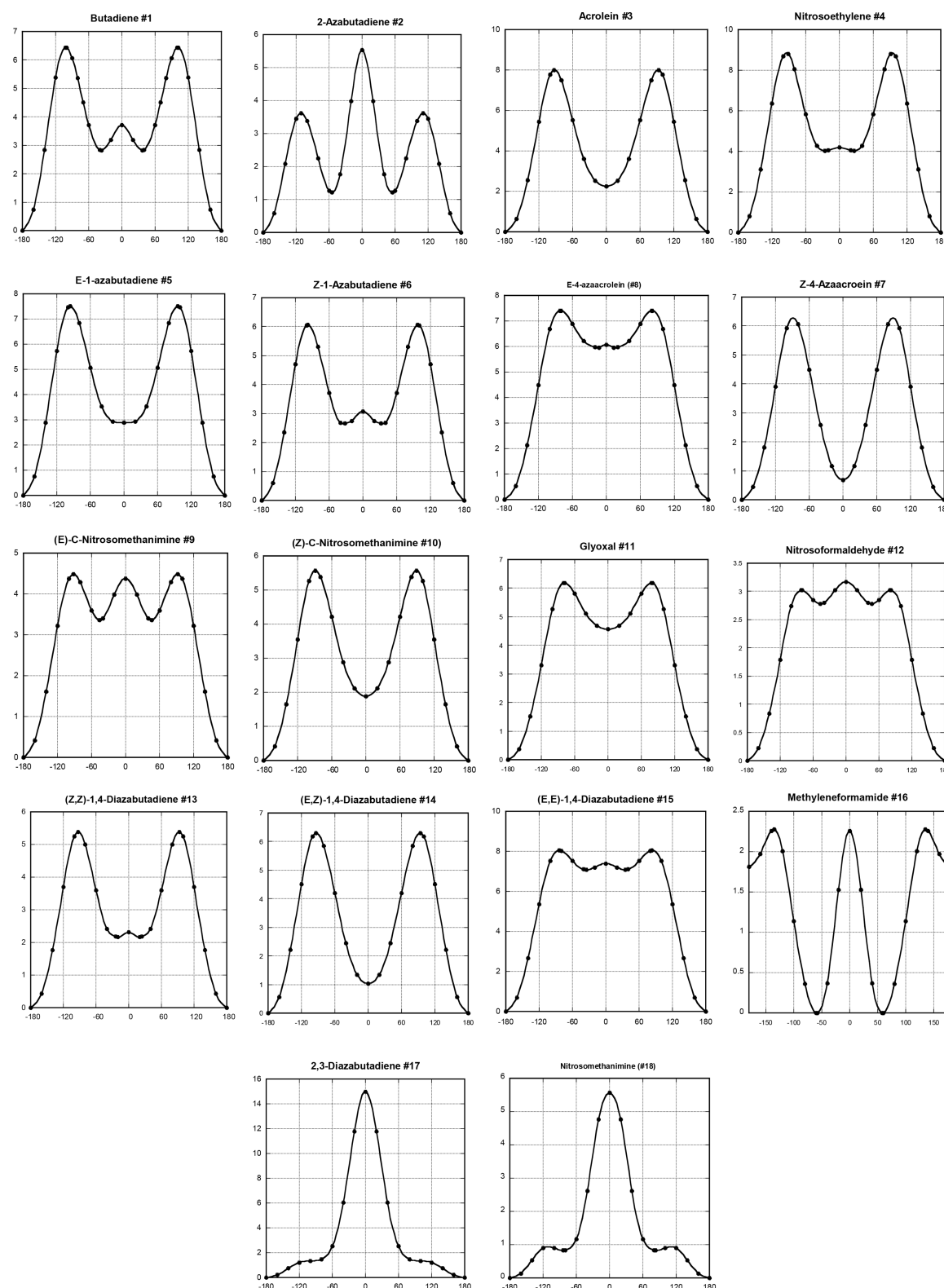


Figure 5. Rotational profiles for heterodienes. The x axis is the torsion angle in degrees, and the y axis is the relative energy (kcal/mol).

The Fourier decomposition for the MP2/aug-cc-pVTZ calculation (Table 1) agrees well with the more expensive CCSD(T)/ANO1 level of theory for butadiene (Table 2). The agreement with the Fourier components of the preferred torsional potential of Boopalachandran et al.³ is also quite good, with the most important (first through third order) terms differing only by a few percent, and certainly well within the

spread of the three sets of parameters presented in Table 4 of ref 3. We recognize that a fit to this type of functional form may not give an immediately useful result, but it is worth noting that describing the torsional potential in this way can account for both the shifted *cis*–*trans* transition state angle and the *gauche* vs *cis* stabilization, which is not the case when we invoke H···H repulsion, for example. A simple hypothesis is then that the 1-fold

Table 1. Results of a Fourier Analysis for the Torsional Potential Energy Functions

structure	terms (kcal/mol)				
	1-fold	2-fold	3-fold	4-fold	constant
butadiene (#1)	1.40	−4.35	2.36	0.74	3.60
2-azabutadiene (#2)	1.97	−0.32	3.28	0.84	2.39
acrolein (#3)	1.65	−6.76	0.72	0.93	4.08
nitrosoethylene (#4)	2.52	−6.58	1.77	1.23	4.81
(E)-1-azabutadiene (#5)	1.59	−5.98	1.43	0.72	4.07
(Z)-1-azabutadiene (#6)	1.42	−4.40	1.69	0.83	3.31
(Z)-4-azaacrolein (#7)	0.86	−5.84	−0.15	0.67	2.97
(E)-4-azabutadiene (#8)	5.59	−4.21	0.41	0.62	4.81
(E)-C-1-azamethanimine (#9)	3.15	−2.28	1.22	0.65	3.01
(Z)-C-nitrosomethanimine (#10)	1.71	−4.54	0.20	0.63	2.94
glyoxal (#11)	4.67	−3.56	−0.15	0.51	3.84
nitrosoformaldehyde (#12)	2.80	−1.35	0.36	0.36	2.10
(Z,Z)-1,4-diazabutadiene (#13)	1.42	−4.19	0.85	0.84	2.83
(E,Z)-1,4-diazabutadiene (#14)	0.55	−5.72	0.56	0.59	3.10
(E,E)-1,4-diazabutadiene (#15)	6.38	−4.27	1.04	0.60	5.53
methyleneformamide (#16)	−1.24	1.23	1.49	0.14	1.30
2,3-diazabutadiene (#17)	10.28	5.94	4.13	1.55	3.65
nitrosomethanimine (#18)	3.93	1.96	1.69	0.43	1.63

Table 2. Comparison of V_n Terms for Butadiene from Experiments and Calculations

source	1-fold	2-fold	3-fold	4-fold	5-fold
experiment, ref 3	1.33	4.44	2.20	0.64	0.06
calculation, ref 5	1.45	4.43	2.11	0.61	0.07
calculation, ref 1	1.39	4.16	3.11	0.55	0.10
MP2/aug-cc-pVTZ	1.38	4.34	2.36	0.75	0.12

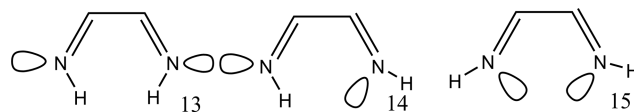
term represents a repulsion that smoothly increases on going from 180° to 0°, the 2-fold term represents the conjugative interaction between the two double bonds, but the 3-fold term remains something that needs to be examined further. To better appreciate the role of these terms, Figure 6 shows the components of the energies for all 18 compounds in this study. The constant term that makes the sum of all terms equal to the calculated torsional potential was left out for clarity in the small plots. Larger plots that include the constant may be found in the Supporting Information.

To see if the terms in Table 1 may be meaningful, it seems appropriate to examine each of them individually. Table 3 lists the 1-fold terms in order of changing size.

The one-fold term for butadiene is 1.40 kcal/mol. There is a repulsive interaction in the *cis*-form as shown by the increase in C—C—C angle from 123.6° in the *trans* form to 126.3° in *cis*. It must be at least 0.7 kcal/mol, the difference in energy between *cis* and *gauche*, and probably is somewhat larger since the *gauche* form is not free of steric effects. Thus, 1.40 kcal/mol seems reasonable and, in fact, is in good agreement with the estimate in ref 1. 2-Azabutadiene (2) has a C—N—C bond angle of 119.8°, considerably smaller than for butadiene, bringing the terminal atoms closer together. Its 1-fold term is accordingly larger, 1.97 kcal/mol. The larger value for acrolein (3), 1.65 kcal/mol might be attributed to repulsion between the oxygen lone pairs and the terminal methylene group, and its increase with nitrosoethylene (4), 2.52 kcal/mol can be attributed to the smaller C—N—O angle, 113.8°.

The smaller 1-fold term for 4-azaacrolein (7), 0.86 kcal/mol, is probably due to the stabilization of the *cis* form by a hydrogen bond between the NH and the O. If the hydrogen is rotated to the other side as with 8, there will be repulsion between the lone pairs at N and O giving a large value (5.59 kcal/mol). The large value for glyoxal (11), 4.67 kcal/mol, must be due to the repulsion between the oxygens both because of the partial negative charge at O and their lone pairs.

The group of 1,4-diazabutadienes, 13, 14, and 15, show an interesting difference in 1-fold terms:



The 1-fold terms are 1.42, 0.55, and 6.38 kcal/mol, respectively. There can be some hydrogen bonding in 14 that would reduce the repulsive interaction present in 1, and 13 has a 1-fold term similar to that in 1. The large increase found with 15 could be due to repulsion between the lone-pairs. The largest 1-fold term is found with 2,3-diazabutadiene (17), 10.28 kcal/mol, where the nitrogen lone-pairs at the single bond will repel each other in the *cis* form. It can be seen that the one-fold terms give a semiquantitative estimate of the 0° repulsion for these compounds.

The 2-fold terms are summarized in Table 4 and are given in order of decreasing absolute values. The value for butadiene (1), 4.35 kcal/mol, is close to the value commonly used. Kistiakowsky³ made use of the difference in gas-phase hydrogenation energies of butadiene and 1-butene to derive a value of 3.7 kcal/mol. This value is probably too small since it neglects the differences in bond lengths between the compounds being compared. It should be noted that Janowski et al.⁶ showed that the correct delocalization energy of butadiene requires the consideration of hyperconjugation effects such as that which leads alkyl substitution to stabilize alkenes. They proposed a simple scheme for correcting the Kistiakowsky estimate, and it led to a delocalization energy of 8.3 kcal/mol. It might also be noted that purely theoretical studies have led to an energy this large or larger.⁷

There are few experimental data regarding the other compounds, and they are fairly old with large uncertainties.⁸ Acrolein (3) would be expected to have a significantly larger 2-fold term than butadiene because the strongly polarized carbonyl group will place a significant partial charge on the carbonyl carbon, and it can lead to a stabilizing interaction with the C—C double bond. In accord with expectation it has the largest 2-fold term. At the other end of the scale, 2,3-diazabutadiene (17) is destabilized by the lone pair repulsion in the *cis* form leading the 2-fold term to be reversed from that of most compounds.

The large positive value for 2,3-diazabutadiene (17) indicates that the molecule would prefer ±90° torsion angle to avoid interactions between the nitrogen atoms. Compounds 16 and 18 have similar problems but to a much smaller extent. In the mid-range around butadiene there are no special additional interactions, and so it is expected that they have similar values. It might be reasonable to consider the 2-fold terms to be a first order measure of the classical conjugative interaction, modified in some cases by steric or Coulombic effects.

We may now turn to the 3-fold terms that are given in order of increasing values in Table 5. It might be noted that the first entry, glyoxal, would be expected to have a significant positive charge at C2 and C3 as a result of the electronegativity of oxygen and that the one at the end of Table 5, 2,3-diazabutadiene, should have a significant negative charge at N2 and N3 because of the

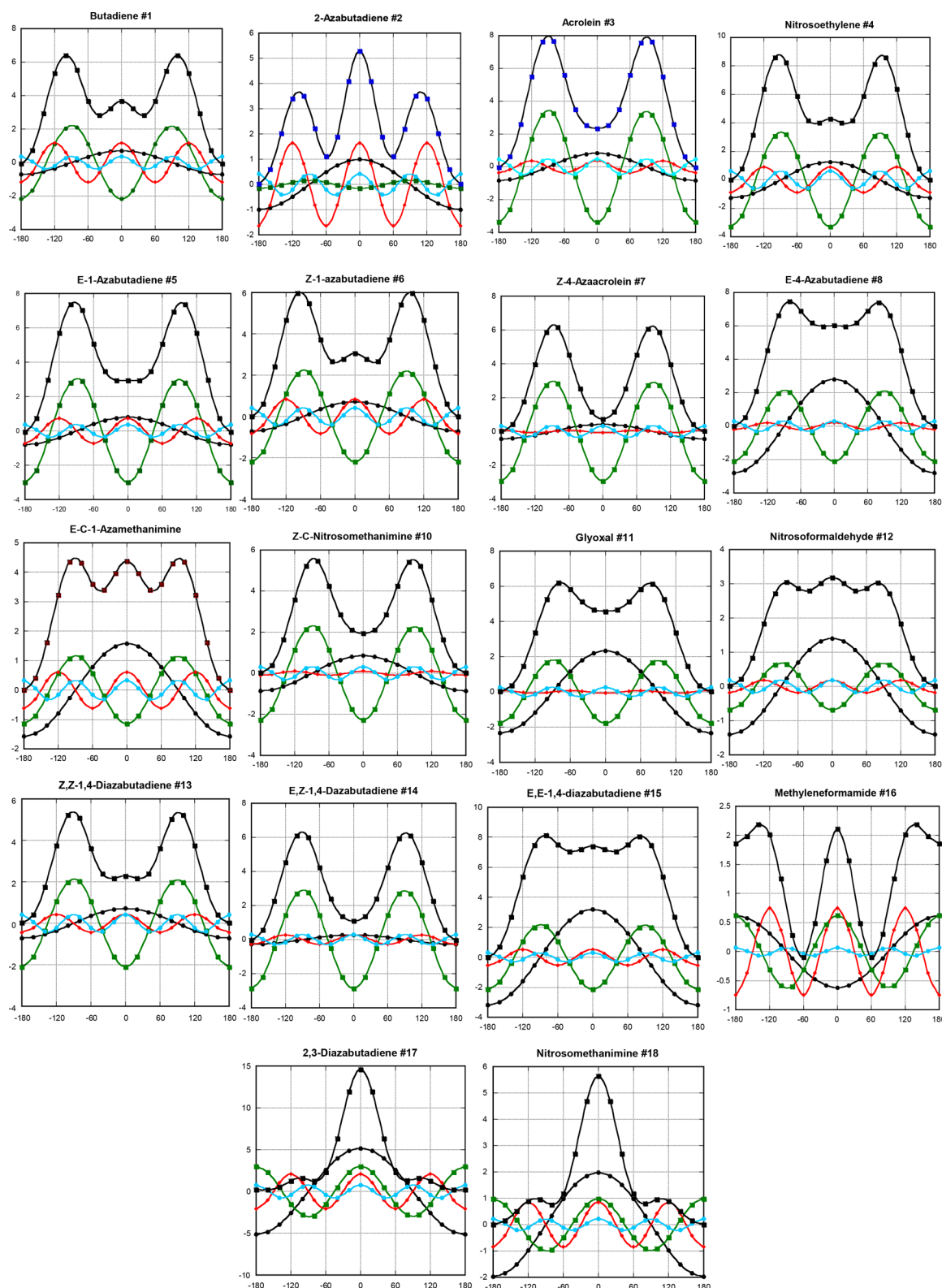


Figure 6. Fourier terms for heterobutadienes. The 1-fold terms are shown in black, the 2-fold are in green, the 3-fold are in red, and the 4-fold are in light blue. The sum including the constant term (upper curve) is given in black. The x axis is the torsion angle, and the y axis gives the relative energies, kcal/mol.

electronegativity of N. These findings suggested that the 3-fold terms might be generally related to the charge at the atoms forming the single bond and led us to calculate the Hirshfeld charges⁹ at atoms 2 and 3 of the compounds in the *cis* forms. They are given in the Table 4. A plot of the average charge against the 3-fold terms is shown in Figure 7.

Table 3. One-Fold Terms in Order of Increasing Size

name	no.	1-fold
methyleneformamide	16	-1.24
(<i>E,Z</i>)-1,4-diazabutadiene	14	0.55
(<i>Z</i>)-4-azaacrolein	7	0.86
butadiene	1	1.40

Table 3. continued

name	no.	1-fold
(Z)-1-azaacrolein	6	1.42
(Z,Z)-1,4-diazabutadiene	13	1.42
(E)-1-azabutadiene	5	1.59
acrolein	3	1.65
methyleneformamide	10	1.71
(E,Z)-1,4-diazabutadiene	2	1.97
(Z)-4-azaacrolein	4	2.52
nitrosoformaldehyde	12	2.80
(E)-C-nitrosomethanimine	9	3.15
N-nitrosomethanimine	18	3.93
glyoxal	11	4.67
(E)-4-azaacrolein	8	5.59
(E,E)-1,4-diazabutadiene	15	6.38
2,3-diazabutadiene	17	10.28

Table 4. Two-Fold Terms in Order of Decreasing Magnitude

name	no.	2-fold ^a
acrolein	3	6.76
nitrosoethylene	4	6.58
(E)-1-azabutadiene	5	5.98
(Z)-4-azaacrolein	7	5.84
(E,Z)-1,4-diazabutadiene	14	5.72
(Z)-C-nitrosomethanimine	10	4.54
(Z)-1-azabutadiene	6	4.40
(E,E)-1,4-diazabutadiene	15	4.27
butadiene	1	4.35
(Z,Z)-1,4-diazabutadiene	13	4.19
(E)-4-azaacrolein	8	4.40
glyoxal	11	3.56
(E)-C-nitrosomethanimine	9	2.28
nitrosoformaldehyde	12	1.35
2-azabutadiene	2	0.32
methyleneformamide	16	-1.23
N-nitrosomethanimine	18	-1.96
2,3-diazabutadiene	17	-5.94

^aThe calculated values have been multiplied by -1 for convenience in the discussion.

It is remarkable to find such a good correlation between the averages of the Hirshfeld charges at atoms 2 and 3 and the

magnitude of the 3-fold term. The values being averaged sometimes have similar magnitude, but in other cases they are quite different, and the length of the single bond is not taken into account, but still the correlation works. The finding that the 3-fold terms are responsible for the *trans/gauche* transition state torsional angle of 101.7°, and its energy being 2 kcal/mol greater than the conjugation energy, along with the results in Figure 7 indicate that the 3-fold terms have physical significance. While it is still not entirely clear what the origin of the 3-fold terms is, we propose a potential explanation in the next section.

With regard to the 4-fold terms: although just the first three terms give relative energies that are close to the calculated results (see Figure S3 in the Supporting Information), there are small differences that are corrected by the 4-fold terms (Figure 6 and Figure S4). A plot of these terms against the charges at atoms 2 and 3, as in Figure 7, gives no correlation.

■ EXPLORATION OF 1,4 π -INTERACTIONS

The 1-fold and 3-fold terms of the Fourier expansions are not straightforward to rationalize. Together they reveal a high energy for the *s-cis* form relative to *s-trans*, as well as intermediate energies for structures with a dihedral angle of ~60°. Using butadiene as an example, these factors cause the *s-cis* form to be a local maximum, lead to a local minimum at 37°, and push the overall maximum past 90° to 102°. The seemingly obvious explanation, repulsion between the inward facing hydrogen atoms, falls short upon closer examination, both because the expected magnitude of the effect is too small at the interatomic distances actually observed and because the effect should be entirely absent in the vicinity of 90°.

If some other factor destabilized structures in the range 0° to approximately 45°, and somewhat stabilized structures in the range 45° to 90°, that could account for the observed potential energy function. Such a factor would probably turn up primarily in the 1-fold and 3-fold terms of the Fourier expansion. What such factor is conceivable?

One possibility is that π -interactions between the terminal positions are significant and can be of either Hückel or Möbius topology¹⁰ depending upon the dihedral angle. In the *s-cis* form, 1,4 interaction would perturb the π -system in the direction of Hückel antiaromaticity and therefore destabilize the molecule.

Table 5. Three-Fold Terms in Order of Increasing Values^a

name	no.	3-fold	q_2	q_3	q_{avg}
glyoxal	11	-0.15	0.1361	0.1361	0.1361
(Z)-4-azaacrolein	7	-0.15	0.1370	0.0420	0.0895
(Z)-C-nitrosomethanimine	10	0.20	0.0704	0.0291	0.0498
nitrosoformaldehyde	12	0.36	0.1624	0.0222	0.0923
(E)-4-azaacrolein	8	0.41	0.1315	0.0466	0.0891
(E,Z)-1,4-diazabutadiene	14	0.56	0.0423	0.0522	0.0473
acrolein	3	0.72	-0.0477	0.1268	0.0396
(Z,Z)-1,4-diazabutadiene	13	0.85	0.0495	0.0495	0.0495
(E,E)-1,4-diazabutadiene	15	1.04	0.0454	0.0454	0.0454
(E)-C-nitrosomethanimine	9	1.22	0.0192	0.0713	0.0453
(E)-1-azabutadiene	5	1.43	-0.0462	0.0478	0.0008
methyleneformamide	16	1.49	-0.1654	0.1661	0.0004
N-nitrosomethanimine	18	1.69	-0.1653	0.0987	-0.0333
nitrosoethylene	4	1.77	-0.0186	0.0114	-0.0036
(Z)-1-azabutadiene	6	1.69	0.0462	-0.0478	0.0008
butadiene	1	2.36	-0.0378	-0.0378	-0.0378
2-azabutadiene	2	3.28	-0.0022	-0.1481	-0.0752
2,3-diazabutadiene	17	4.13	-0.1150	-0.1150	-0.1150

^a q_1 and q_2 are the Hirshfeld charges (e) for the atoms forming the single bond in the *cis* conformers, and q_{avg} is the average of the two values.

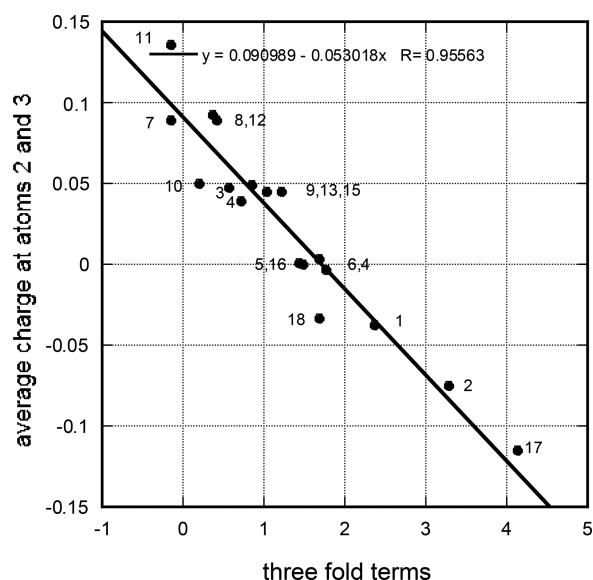


Figure 7. Relationship between the values of the 3-fold terms and the average charge at atoms 2 and 3.

With $\sim 45^\circ$ or more of twisting, however, the 1,4 overlap would be of Möbius topology and, thus, stabilizing for a 4-electron π -system. At dihedral angles much greater than 90° , the interaction would presumably be absent altogether. These 1,4 π -interactions

could account for the unusual behavior of butadiene: they would destabilize the *s-cis* form over and above what is expected for the $H\cdots H$ repulsion and also provide some stabilization for a gauche structure. If the Möbius stabilizing interaction were still somewhat in operation at 90° , as seems reasonable to suppose, that could also account for the overall energy maximum occurring at a larger angle, 102° , at which point the stabilization is likely negligible.

Using simple Hückel theory,¹¹ Figure 8 provides a qualitative analysis of how interaction between carbons 1 and 4 would be expected to affect the π MO energies. The analysis pertains to butadiene, but similar arguments could be made for the other heterobutadienes. The top portion shows what happens in the planar *s-cis* conformation. With no interaction assumed between the terminal positions, the conventional Hückel MO energies for butadiene are obtained. If full overlap between the terminal carbons is postulated, as in cyclobutadiene, the set of energies at the far right is obtained. The net result is a large increase in the energy difference between π_1 and π_2 , and also a substantial increase in the total π energy (recall that β is a negative number in Hückel theory). If there is just a small amount of overlap between carbons 1 and 4, say 10% as much as between the bonded pairs (1 to 2, 2 to 3, and 3 to 4), then the effect is qualitatively similar but proportionally smaller. The $\pi_2 - \pi_1$ energy difference and the total π energy still both increase.

The bottom portion of Figure 8 shows what happens in a twisted conformation having a dihedral angle of, say, 60° . If full *antibonding* overlap between the terminal carbons is postulated,

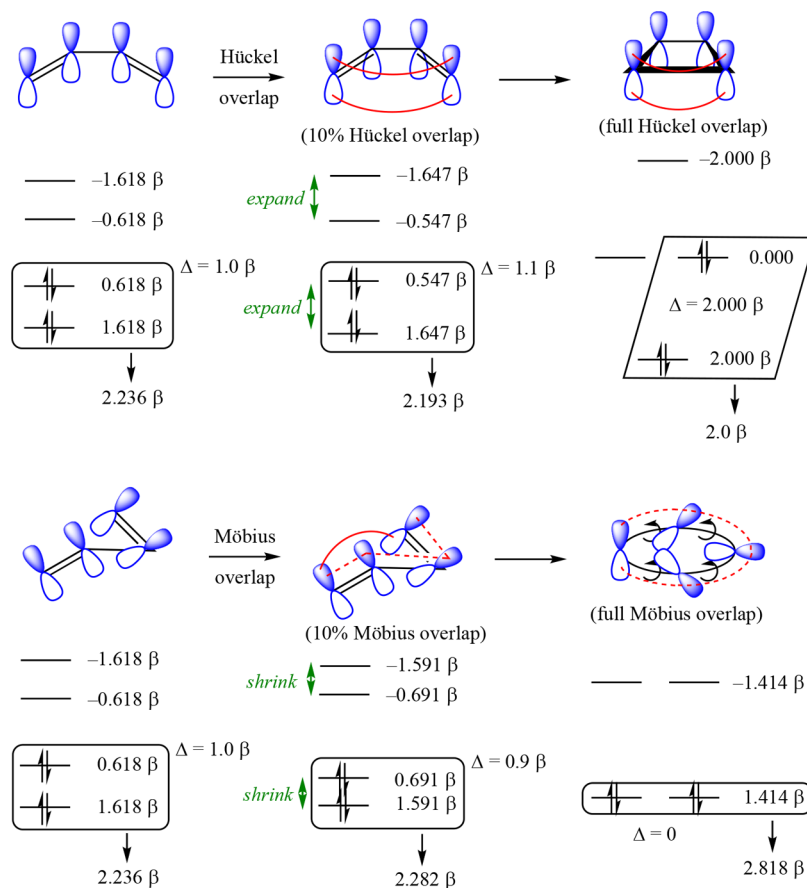


Figure 8. Qualitative analysis of the effect of π -overlap between the terminal positions of butadiene using Hückel theory. (A) Effect of overlap in the *s-cis* conformation. The far left shows butadiene with no overlap postulated between the terminal carbon atoms. The far right depicts the extreme case of complete π -overlap that leads to cyclobutadiene, a Hückel antiaromatic compound. Partial overlap (10%) leads to an intermediate situation (middle). (B) Effect of overlap in a twisted (*gauche*) conformation. The far left shows butadiene with no overlap postulated between the terminal carbon atoms. The far right depicts the extreme case of complete antibonding overlap, leading to a Möbius aromatic structure. Partial overlap (10%) leads to an intermediate situation (middle).

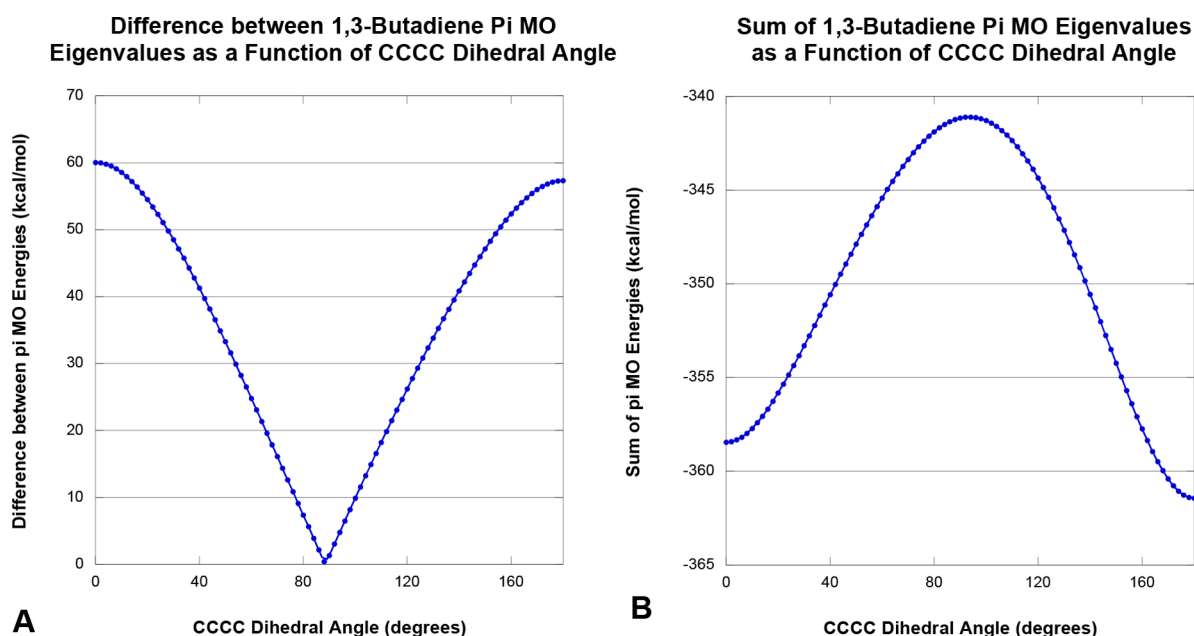


Figure 9. Variation of butadiene π MO (HOMO and HOMO–1) eigenvalues (computed at B3LYP/aug-cc-pVTZ) as a function of dihedral angle, for a rigid rotation starting with the MP2/aug-cc-pVTZ geometry for *s-trans*. (A) Plot of $\pi_2 - \pi_1$ as a function of dihedral angle. The difference is greater when conjugation is stronger, and therefore, as expected, the value is at a maximum in the planar conformations and at a minimum in the 90° structure. However, the eigenvalue difference is greater in the *s-cis* than in the *s-trans* conformation. (B) Plot of $\pi_1 + \pi_2$ as a function of dihedral angle. The π energy is lower when conjugation is stronger, and therefore, as expected, the value is at a minimum in the planar conformations and at a maximum in the 90° structure. However, the π -energy is lower in the *s-trans* than in the *s-cis* conformation.

as in an ideal Möbius system, the set of energies at the bottom far right is obtained. The net result is that π_1 and π_2 become degenerate, and the total π energy decreases substantially. If there is just a small amount of antibonding overlap between carbons 1 and 4, say 10% as much as between the bonded pairs, the effect is in the same direction but proportionally smaller. The $\pi_2 - \pi_1$ energy difference and the total π energy both decrease, relative to when there is no interaction.

The MO eigenvalues (energies) provide some evidence to support the presence of 1,4 π -interactions,¹² in that these eigenvalues behave exactly in the manner predicted in Figure 8. Since the eigenvalues are highly sensitive to even small changes in bond lengths and bond angles (although in a mutually compensating manner), it is necessary to use a rigid rotation in such an analysis. Therefore, we used the MP2/aug-cc-pVTZ optimized geometry of the *s-trans* conformation of butadiene as a starting point, and then conducted calculations at successive geometries obtained by incrementing the CCCC dihedral angle by 2° at a time, while holding all other geometric parameters fixed. At each geometry, a B3LYP/aug-cc-pVTZ single point calculation was used to evaluate the MO eigenvalues. The HOMO and the HOMO–1 correspond to the orbitals π_2 and π_1 , respectively.¹³

Figure 9 illustrates how the π MO eigenvalues respond to the bond rotation. Figure 9A shows the value of $\pi_2 - \pi_1$ as a function of dihedral angle, while Figure 9B shows the value of the sum, $\pi_1 + \pi_2$. Both values depend strongly on the extent of conjugation. Accordingly, $\pi_2 - \pi_1$ reaches a minimum (almost zero) at 90° while having maxima at 0° and 180° . Conversely, $\pi_1 + \pi_2$ reaches a maximum at 90° , when there is no conjugation, and has minima at 0° and 180° . However, the curves are not symmetric. That is, the rotation from 90° to 180° is not quite equivalent to the rotation from 90° to 0° .

Figure 10 depicts the differences. In blue is shown how $\pi_2 - \pi_1$ differs for $90^\circ \rightarrow 0^\circ$, compared to $90^\circ \rightarrow 180^\circ$. That is, for each dihedral angle X° , what is plotted is the value of $\pi_2 - \pi_1$ for X° ,

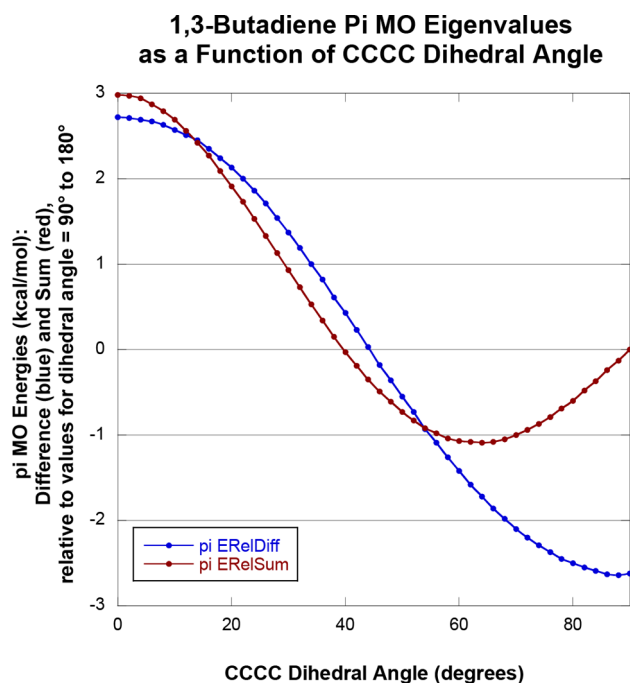


Figure 10. Difference in the behavior of the π MO eigenvalues of butadiene for the rotation $90^\circ \rightarrow 0^\circ$, compared to $90^\circ \rightarrow 180^\circ$. This plot shows the same essential data as Figure 9, except depicted in such a way as to emphasize the subtle but important difference in going from 90° to either *s-cis* or *s-trans*. Each point represents the value of the given quantity for a dihedral angle of X° , minus the value of the same quantity for a dihedral angle of $(180 - X)^\circ$. The blue curve represents $\pi_2 - \pi_1$, while the red curve represents $\pi_1 + \pi_2$.

minus that for $(180 - X)^\circ$. The red curve shows the same comparison for $\pi_1 + \pi_2$. The curves provide two important observations. First, the effects are repulsive (positive for both quantities)

in the region 0–40° but attractive (negative for both quantities) in the region 45–90°. Second, the magnitude of the effect is on the order of ± 3 kcal/mol. Both observations accord well with the overall potential energy function calculated for butadiene, especially if one takes into account that the true energetic consequences are likely moderated by relaxation of the molecular geometry.

The postulated π -interactions are also consistent with the relationship between charge and the 3-fold term that is depicted in Figure 7. This relationship can be summarized as the following three effects on the magnitude of the 3-fold term:

- It is reduced when nitrogen is in an outer (1 and/or 4) position.
- It is reduced even more when oxygen is in an outer position.
- It is enhanced when nitrogen is in an inner (2 or 3) position.

Since p -orbitals on nitrogen are more compact than those on carbon, the 1,4 π -overlap should be less when nitrogen, instead of carbon, is in a terminal position. That replacement would in turn reduce the magnitude of the 1,4 π -interaction, and thus the 3-fold term. A similar argument holds for oxygen, only more strongly. On the other hand, if nitrogen is in an inner position, the bond angle is reduced. That brings the 1 and 4 positions closer together, so that π -overlap and the 3-fold term increase.¹⁴

An additional observation also supports the notion of π -repulsion in *s-cis* butadiene. One would expect compression of the CCC bond angle to increase π repulsion between carbons 1 and 4, and therefore to raise the values of both $\pi_2 - \pi_1$ and $\pi_1 + \pi_2$. That is indeed the case. The values of both $\pi_2 - \pi_1$ and $\pi_1 + \pi_2$ rise by 4–10 kcal/mol as the bond angle decreases from 130° to 110° (Figure S2, Supporting Information).

SUMMARY

The bond rotation profiles for 18 dienes have been calculated at the MP2/aug-cc-pVTZ level and have been examined by carrying out a sixth order Fourier analysis. The first order terms were found to be reasonably associated with a smooth change in energy on going from a dihedral angle of 180° to 0°. The second order terms would naturally be associated with the delocalization energy of the diene, and in the case of butadiene, it leads to a value of 4.3 kcal/mol that is close to the estimate derived from heats of hydrogenation. Some of the changes with respect to butadiene could be ascribed to additional opportunity for delocalization such as with acrolein. The third order terms were found to be related to the sum of the atomic charges of the atoms forming the central single bond. Although the origin of the 3-fold terms is still unknown, in the case of butadiene this term shifts the trans/gauche transition state from the nominal 90° to 101.7° and increases the transition state energy to 6.2 kcal/mol. A 1,4 π -interaction appears consistent with the available data at this time and could account for the observed effects.

CALCULATIONS

All of the calculations were carried out using Gaussian 16.¹⁵

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b01085.

Tables of aug-cc-pVTZ atomic coordinates for all of the trans conformers used as starting points for scans, table of energies vs torsion angles for butadiene, full-sized plots

corresponding to Figures 5 and 6 and the results for a five-term Fourier analysis, and figure showing π -orbital eigenvalues as a function of CCC bond angle in butadiene (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank G. B. Ellison, S. Kozuch, and A. Milo for helpful discussions

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changes going around the cycle. This is the topology for a normal cyclic polyene (e.g., benzene, etc.). In Möbius topology, on the other hand, the geometry is such that at least one sign change must occur as one travels around the cycle, and so each MO has an odd number of sign changes around the cycle. Möbius topology can occur if there is a half-twist of the nodal plane of the atomic p -orbitals as one goes around the cycle or, as in this case, if there is some degree of helicity such that the top face of one end of a polyene overlaps with the bottom face of the other end.

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(12) Unlike the occupied MO energies of a Hückel calculation, the sum of the eigenvalues of the occupied MO's in an ab initio calculation does not yield to total electronic energy. Nonetheless, the orbital eigenvalues do have some meaning, and one can ask whether, under some perturbation, they behave qualitatively in the manner predicted.

(13) This assignment is exact in the 180° and 0° conformations, but only qualitative in the other conformations, for which there is no absolutely strict σ/π separation.

(14) The CCC bond angle of *s-cis* butadiene is 126.3° , but for 2-azabutadiene the CNC angle is only 119.8° . The result is that C_1 and C_4 are separated by 3.05 Å in butadiene but only 2.89 Å in 2-azabutadiene.

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