6842 *J. Org. Chem.* **1999,** *64,* 6842−6848

# Study of the Electrocyclization of (*Z*)-Hexa-1,3,5-triene and Its Heterosubstituted Analogues Based on Ab Initio and DFT Calculations

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*Received June 1, 1999*

A comprehensive theoretical study of the electrocyclization of (*Z*)-hexa-1,3,5-triene and its heterosubstituted analogues (*E*,*Z*)-[(2*Z*)-2,4-pentadienylidene]amine and (2*Z*)-2,4-pentadienal to 1,3-cyclohexadiene, 1,2-dihydropyridine, and 2*H*-pyran, respectively, was conducted. The study included a conformational analysis of the reactants, locating transition structures and optimizing the closed products. The energy, geometry, and vibrational frequencies of all structures were calculated at the MP2/6-31G** and B3LYP/6-31G** levels. Also, electron correlation was improved by single-point calculations using the QCISD(T) and MP4SDTQ methods. The results were consistent with experimental values and accurately reproduced the decrease in activation energy of the heterosubstituted derivatives relative to the parent compound. Complementary natural bond orbital (NBO) computations helped to interpret such a decrease. The involvement of a lone pair of the nitrogen or oxygen atom appears to facilitate the interaction between the terminal atoms that bond to each other to close the cycle. In regard to the enthalpies of the electrocyclization reactions studied, the results reveal a clear-cut trend to instabilization in the closed forms when the terminal methylene groups are replaced with the heteroatoms. Thus, the process is clearly exothermic for hexatriene, much less so for the pentadienimine, and even slightly endothermic for the pentadienal.

## Introduction

The interconversion of (*Z*)-hexa-1,3,5-triene to 1,3-cyclohexadiene (Figure 1, X = $CH_2$) is the most simple example of a thermal, disrotatory, six-electron electrocyclization allowed for by the Woodward−Hoffmann rules.[1] This type of reaction, in addition to the corresponding photochemical conrotatory interconversion, is involved in the biosynthesis of vitamin D,[2−5] as well as in the basic reactions that define the underlying mechanisms for the thermochromic and photochromic behavior of fulgides and fulgimides,[6,7] [10]-annulenes,[8] and diarylethylenes.[9]

This electrocyclic thermal reaction has been thoroughly characterized in experimental terms. Thus, its kinetic parameters have been determined by two research groups;[10,11] also, the geometric parameters for the reactant[12] and product[13,14] have been derived from electron diffraction studies.

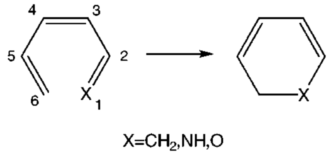

**Figure 1.** Reaction schemes for the four electrocyclizations studied.

Both the reactant and the electrocyclization process have also been studied theoretically, using semiempirical[15−17] and ab initio calculations[18−25] of variable complexity. All these computations have confirmed the concerted disrotatory mechanism predicted by Woodward and Hoffmann.[1] Notwithstanding their shortcomings, semiempirical (MINDO/2 and MINDO/3) calculations reproduce, with acceptable errors, the experimental activation energy (29.9 ± 0.5 kcal/mol).[10,11] With ab initio calculations, the activation energy as calculated by the Hartree−Fock method[18,24] is overestimated relative to the

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10.1021/jo990881w CCC: $18.00

experimental value—as is often the case. Also, as usually happens, introduction of electronic correlation at the MP2 level yields a too small activation energy.[20,24] Improving the results entails refining the correlation treatment by using more sophisticated theoretical levels. On the basis of the MP2/6-31G** geometry and energy computations at the MP4SDTQ/6-311G** level corrected for the zero-point vibrational energy (ZPE) and thermal energies, Jiao and Schleyer[25] obtained results highly consistent with the experimental value. Using DFT calculations at the B3LYP/6-311+G* level, these authors obtained similar results but with substantial computational savings. This was not the case with the experimental value for the enthalpy[26,27] of this clearly exothermic reaction; in fact, DFT computations led to a value slightly worse than that provided by fourth-order Møller–Plesset calculations.

Similar transformations in compounds where one terminal methylene is replaced with an isoelectronic oxygen or nitrogen atom (Figure 1) are the basis for the photochromic and thermochromic behavior of various types of compounds such as spiropyrans,[28] chromenes,[29] spirooxazines,[30] and dihydroquinolines,[31] among others. On the basis of experimental estimates, the replacement of the methylene group has a marked effect on the electrocyclization process; in fact, the activation energy decreases by about 10 kcal/mol, both in the conversion of (*E*)-[(2*Z*)-2,4-pentadienylidene]amine into 1,2-dihydropyridine[32] and in that (2*Z*)-2,4-pentadienal into 2*H*-pyran.[32–34] It should be noted that [(2*Z*)-2,4-pentadienylidene]amine can occur in a *Z* or *E* configuration depending on the position of the imine hydrogen atom with respect to the $N_1{=}C_2$ double bond. Experimental estimates of the activation energy, 17.5–22.5 kcal/mol, correspond to the more stable configuration (*E*). The potential cyclization of the *Z* configuration, for which no experimental data are available, is substantially complicated by the fact that the $N_1{=}C_2$ bond must rotate outward in order to form 1,2-dihydropyridine, the product of both configurations.

Unlike hexatriene, the cyclization of its analogues has scarcely been studied. Semiempirical and ab initio calculations on the pentadienal predict a similar stability for the reactant and product. In MNDO,[35] MINDO/3,[17] and DFT(BLYP) computations,[36] the open-ring form is slightly favored; in HF calculations, the stability sequence is strongly influenced by the particular basis set used; finally, MP2 single-point calculations predict a higher stability in the closed-ring form (2H-pyran).[37] On the basis of these calculations, the activation energy for the electrocyclization process varies over a wide range (from a little over 10 kcal/mol to almost 50 kcal/mol).

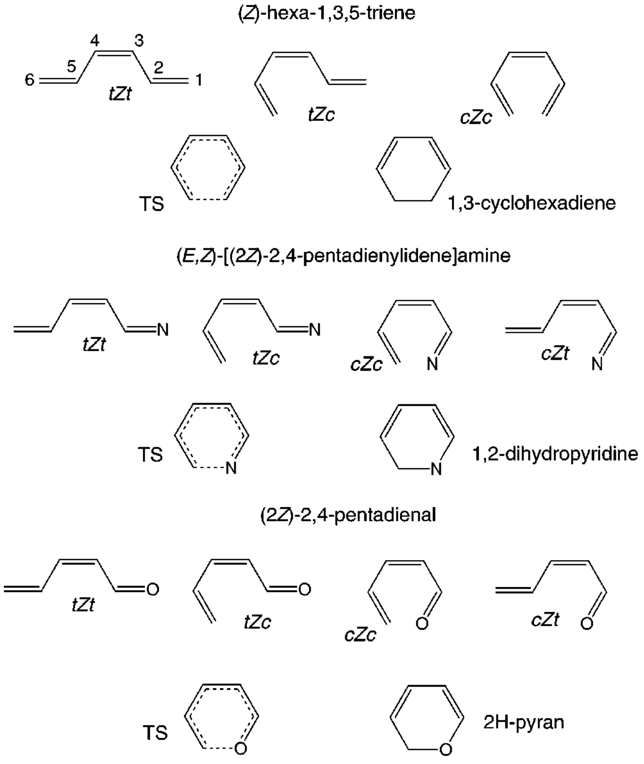

**Figure 2.** Structures examined. All were fully optimized at the MP2/6-31G** and Becke3LYP/6-31G** levels. Their analytical frequencies were also calculated.

Reported theoretical studies on the cyclization of (*E*)-[(2*Z*)-2,4-pentadienylidene]amine are essentially limited to those of Pichko et al. at the MINDO/3 semiempirical level.[17] These authors predicted an activation energy very similar to that for the pentadienal but also a clearly exothermic reaction (as for the hexatriene cyclization).

To systematically examine and compare the above-mentioned electrocyclic reactions, a study involving the conformational analysis of the reactants, locating transition states, and optimizing the products was conducted.

## Computational Details

The geometries of all stationary points (Figure 2) were fully optimized with the Gaussian 94 software package,[38] using the standard 6-31G** basis set and the second-order Møller–Plesset perturbation theory (MP2) to account for the electron correlation energy. All points were characterized as minima or saddle points by calculation of the harmonic vibrational frequencies, using analytical second derivatives. Single-point energy calculations were performed on all MP2/6-31G** structures through quadratic CI computations,[39] including single and double substitutions, and the triples correction (QCISD(T)). Single-point calculations were also obtained with the fourth-order Møller–Plesset correlation energy correction,[40,41] including single, double, triple, and quadruple sub-

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stitutions (MP4SDTQ). Such energies were corrected for zero-point vibrational energies (ZPE) obtained from MP2 frequencies scaled by an empirical factor of 0.9608 to correct for the harmonic approximation.[42]

Recently, Houk et al.[43] showed calculations of the density functional theory (specifically, the Becke3LYP functional)[44,45] to provide high-quality results for pericyclic reactions, with transition structures and activation energies very similar to those obtained with sophisticated—and computationally more expensive—ab initio methods. For this reason, in the present work simultaneous computations at the B3LYP/6-31G** level that included all frequencies, also scaled by an empirical factor (0.9806),[42] were performed.

Electron structures were analyzed in the light of the Natural Bond Orbital (NBO) method,[46−48] included in Gaussian 94, using the MP2/6-31G** and B3LYP/6-31G** electron densities.

## Results and Discussion

**Conformational Analysis of the Reactants.** As shown in Figure 2, hexatriene can occur as three conformers if each is considered to be a planar molecule. In the Figure, *t* and *c* denote the s-trans and s-cis conformations, respectively, with respect to the C−C single bonds, and *Z* denotes the cis form (the sole configuration studied in this work) relative to the central C═C double bond. As expected, the three calculation methods used (QCISD(T), MP4SDTQ, and B3LYP) predict that isomer *tZt* will be the most stable (see Table 1) and *cZc* the least. This latter conformer is the precursor for the electrocyclization as it is structurally ready for immediate reaction. In regard to geometries, only *tZt* is absolutely planar (with a $C_{2v}$ symmetry). Because of obvious steric repulsions, both *tZc* and, especially, *cZc*, are markedly nonplanar. Consequently, they should rather be labeled *tZg* and *gZg* (where *g* denotes gauche), following Panchencko et al.[21] As expected, nonplanarity affects almost exclusively the dihedrals that lead to the s-cis conformation in the single bonds; the rest of the molecule remains virtually planar. Thus, the $C_6C_5C_4C_3$ dihedral in *tZc* deviates by 42.9° (MP2) and 37.6° (DFT) from planarity; in *cZc*, both this dihedral and $C_4C_3C_2C_1$ deviate by 47.1° (MP2) and 35.4° (DFT). This latter isomer possesses a helical structure of $C_2$ symmetry.

The MP2 and DFT geometries obtained for the *tZt* isomer are more than acceptably consistent with their experimental electron diffraction data.[12,13] Only the DFT bond angles values exhibit some small differences from their experimental counterparts. Worth special note is the divergent experimental value for the $C_5C_4C_3C_2$ dihedral, 10.13°. However, as shown by Liu and Zhou,[23] the planar equilibrium structure is supported by the fact that the observed spectral features[49−53] are satisfactorily reproduced by the scaled ab initio force field calculated at the planar structure. Around the $C_{2v}$ equilibrium structure, the potential surface is very flat with respect to the torsional motions around both C−C single bonds and the central C═C double bond. As a result, the thermal average of the torsional motions may be responsible for the nonplanarity observed in some experiments.

**Table 1. Calculated Relative Energies (kcal/mol) for the Compounds of Figure 2[a]**

| | | QCISD(T)[b] | MP4SDTQ[c] | B3LYP[d] |
|---|---|---|---|---|
| hexatriene | *tZt* | 0.00 | 0.00 | 0.00 |
| | *tZc* | 2.85 | 2.81 | 3.86 |
| | *cZc* | 7.43 | 7.50 | 9.77 |
| TS | | 32.23 | 30.30 | 30.11 |
| cyclohexadiene | | −15.59 | −16.27 | −12.21 |
| (*E*)-dienimine | *tZt* | 0.00 | 0.00 | 0.00 |
| | *tZc* | 2.59 | 2.60 | 3.68 |
| | *cZc* | 6.11 | 5.87 | 6.23 |
| | *cZt* | 1.57 | 1.36 | 1.31 |
| TS | | 25.94 | 22.11 | 20.58 |
| dihydropyridine | | −5.59 | −6.80 | −6.98 |
| (*Z*)-dienimine | *tZt* | 0.00 | 0.00 | 0.00 |
| | *tZc* | 2.72 | 2.70 | 3.81 |
| | *cZc* | 5.95 | 6.10 | 8.08 |
| | *cZt* | 2.18 | 2.20 | 3.18 |
| TS | | 39.73 | 37.53 | 37.12 |
| dihydropyridine | | −6.07 | −7.20 | −7.19 |
| pentadienal | *tZt* | 0.28 | 0.33 | 0.45 |
| | *tZc* | 2.89 | 2.93 | 3.69 |
| | *cZc* | 5.24 | 5.19 | 4.84 |
| | *cZt* | 0.00 | 0.00 | 0.00 |
| TS | | 24.80 | 22.92 | 21.52 |
| 2H-pyran | | 2.76 | 2.96 | 3.44 |

[a] The values are corrected for zero-point vibrational energies (ZPE). The ZPE was scaled[42] by 0.9608 [(ZPE(MP2/6-31G**) × 0.9608] or by 0.9806 [(ZPE(B3LYP/6-31G**) × 0.9806]. [b] QCISD(T)/6-31G**//MP2/6-31G**. [c] MP4SDTQ/6-31G**//MP2/6-31G**. [d] B3LYP/6-31G**//B3LYP/6-31G**.

As noted in the Introduction, [(2*Z*)-2,4-pentadienylidene]amine occurs in two different configurations of the imine hydrogen atom with respect to the $N_1$═$C_2$ double bond that will henceforward be referred to as (*Z*)-dienimine and (*E*)-dienimine. Each of these configurations can exist in four different conformations, namely three similar to those of hexatriene (*tZt*, *tZc*, and *cZc*) and a fourth, *cZt*, which arises from asymmetry in the molecule. There are thus eight different structures in all (Figure 2). The energies for these structures (Table 1) are very similar to those for hexatriene; thus, *tZt* is the most stable conformation and *cZc* the least, both in the *Z* and *E* configurations. Of the two remaining conformations, *cZt* is slightly more stable than *tZc*; however, the energy difference between them is only appreciable in the *E* configuration. This appears to be a result of the interaction between the nitrogen atom and the hydrogen of $C_5$, which is weak ($d_{N---H}$ is 2.335 Å with MP2 and 2.338 Å with DFT) but leads to a completely planar *cZt*(*E*) conformation. The geometric trends in the *cZt*(*Z*) and *tZc*(*E*,*Z*) conformations are qualitatively and quantitatively similar to the hexatriene case. Thus, nonplanarity affects those dihedrals that result in the s-cis conformations of the single bonds. In regard to the least stable conformations, *cZc*, the (*Z*) configuration adopts a helical spatial arrangement that is very similar to that in

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hexatriene. On the other hand, the geometry of the *cZc*(*E*) conformation differs between DFT and MP2. Both geometries tend to be planar, which also seems to be the result of the N- - -H interaction—with the hydrogen atom of the methylene group in this case. However, while the DFT results suggest absolute planarity, the MP2 results lead to a boat conformation with the following dihedral angles: −37.8° for $C_4C_3C_2C_1$, 1.2° for $C_5C_4C_3C_2$, and 36.4° for $C_6C_5C_4C_3$. The divergence between the DFT and MP2 results, however, is less pronounced than expected; in fact, if a $C_s$ planar symmetry is forced in the MP2 calculations, then a conformation—a transition state as it possesses an imaginary frequency—with an energy only slightly higher than that of the nonplanar minimum (0.94 kcal/mol with QCISD(T) and 0.61 kcal/mol with MP4-SDTQ) is obtained. This suggests the presence of a very flat zone about the $C_s$ symmetry in the MP2 potential hypersurface. The hydrogen bond in this *cZc*(*E*) conformation results in N- - -H distances of 2.106 Å with DFT and 2.233 Å with MP2.

Pentadienal also gives four conformations (viz. *tZt*, *tZc*, *cZc*, and *cZt* (Figure 2)), the energy differences at 0 K among which are shown in Table 1. Unlike hexatriene and (*E*,*Z*)-dienimine, the most stable conformation is not *tZt*, as this is slightly more unstable than *cZt*. The origin of the pronounced stabilization of the latter must be the same as that suggested above for *cZt* in (*E*)-dienimine, viz. a hydrogen-bonding interaction. In this case, the stabilizing effect of the interaction of the oxygen atom with the hydrogen of $C_5$ appears to be stronger, so much so that it alters the stability sequence. As with (*E*)-dienimine, this hydrogen bond also gives rise to an absolutely planar conformation with a $d_{O---H}$ value of 2.291 Å (MP2) or 2.293 Å (DFT). As in the other compounds, *tZt* is planar and *tZc* is substantially nonplanar in the $C_6C_5C_4C_3$ dihedral. The geometry of the least stable conformation, *cZc*, is similar to that of (*E*)-dienimine: the O- - -H interaction induces a trend to planarity, which is only complete with the DFT calculations. The MP2 geometry is of the boat type (the $C_4C_3C_2C_1$, $C_5C_4C_3C_2$, and $C_6C_5C_4C_3$ dihedral angles are −24.7°, 2.4°, and 30.1°, respectively) and possesses an energy virtually identical with that of the MP2 geometry of fixed $C_s$ symmetry: the nonplanar minimum is only 0.07 kcal/mol (QCISD(T)) or 0.08 kcal/mol (MP4SDTQ) more stable. The O- - -H interaction results in $d_{O---H}$ values of 2.051 Å (DFT) and 2.164 Å (MP2).

Regarding the relative energies of the different conformers (Table 1), the DFT results are very similar to those provided by computationally much more expensive methods such as MP4SDTQ and QCISD(T). The differences between the latter two are virtually zero. Overall, the DFT energy differences among conformers are somewhat greater.

On the basis of the geometry of the most stable conformation for each of the compounds studied, the results provided by the DFT and MP2 methods are very similar, with no appreciable differences between the two. In fact, the differences are in the region of thousandths of an angstrom and tenths of a degree. Also, the only appreciable differences between the DFT and MP2 calculations for all the optimized conformations are those in the *cZc* structures of (*E*)-dienimine and pentadienal.

**Analysis of Transition Structures. Activation Energies.** The transition structure for each of the four compounds studied in the electrocyclization process was identified. Figure 3 shows the four structures concerned (MP2 geometry) and the normal vibrational frequency corresponding to the imaginary frequency. As can clearly be seen, the electrocyclization of hexatriene is disrotatory as are those of the other compounds, with the obvious differences arising from their structural peculiarities.

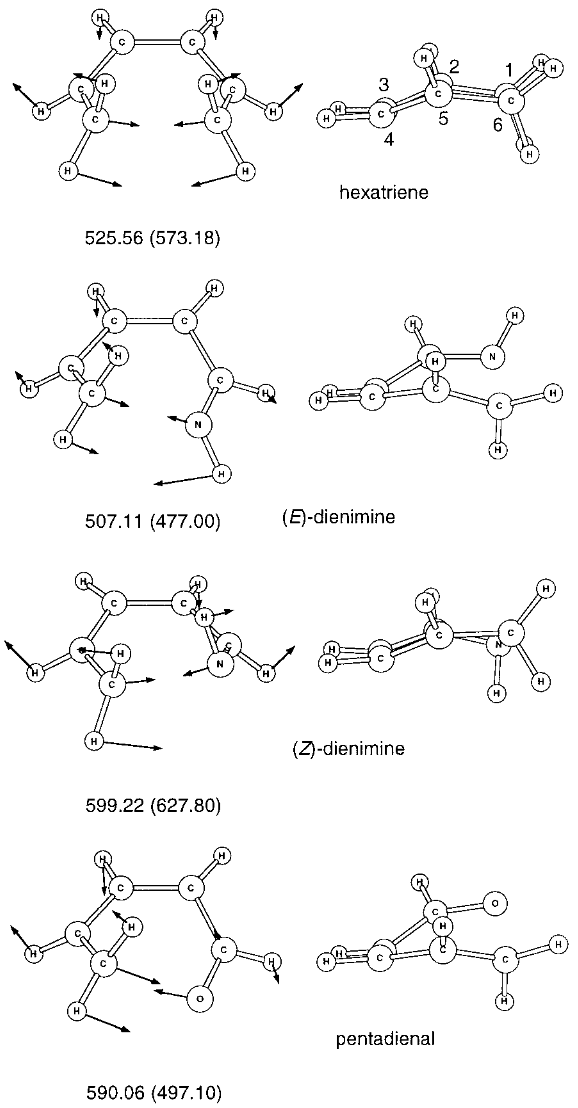

**Figure 3.** Transition structures at the MP2 level and normal mode eigenvectors for the coordinate frequency. The right-hand column shows a side view (profile) of the structures. A virtually identical graph is provided by B3LYP calculations, with no appreciable differences. The value of the imaginary frequency ($cm^{-1}$) is given in each case, with DFT values in parentheses.

The estimated activation energies for the electrocyclization process (see Table 1, which gives the values at 0 K since ZPE correction was applied but the thermal energy at a given temperature was not considered) are reasonably similar with the three computational methods (QCISD(T), MP4SDTQ, and Becke3LYP) and acceptably consistent with the experimental estimates. Relative to the most reliable experimental value, viz. that for hexatriene ($E_a \approx 30$ kcal/mol),[10,11] the QCISD(T) value, 32.23 kcal/mol, was slightly overestimated, even though it was the computationally most expensive to obtain. To account for this fact, the activation energy was calculated in a more accurate manner by adding the thermal (vibrational, rotational, and translational) energies to the

**Table 2. Calculated Activation Energies and Enthalpies of Reaction (kcal/mol) for the Electrocyclization of Hexatriene to 1,3-cyclohexadiene at 400 K**[a]

| | $E_a$ | $\Delta H$ |
|---|---|---|
| experimental | 29.9 ± 0.5[b] | −17.5[c] |
| MP4SDTQ/6-31G*//MP2/6-31G* | 30.4[d] | −17.8[d] |
| MP4SDTQ/6-31G**//MP2/6-31G** | 30.0 | −17.7 |
| MP4SDTQ/6-311G**//MP2/6-31G** | 28.6 | −17.8 |
| QCISD(T)/6-31G**//MP2/6-31G** | 31.9 | −17.0 |
| QCISD(T)/6-311G**//MP2/6-31G** | 30.8 | −17.2 |
| B3LYP/6-31G**//B3LYP/6-31G** | 29.8 | −13.5 |
| B3LYP/6-311+G*//MP2/6-31G* | 30.6[d] | −11.8[d] |
| B3LYP/6-311++G**//B3LYP/6-31G** | 30.4 | −11.3 |

[a] Values are corrected for ZPE and thermal energies (based on scaled frequencies computed at the same level as the corresponding geometric optimization). [b] Reference 10. [c] Estimated using Benson increments, see ref 27. [d] Reference 25.

enthalpies of activation, $\Delta H^{\ddagger}$, and taking into account that $E_a = \Delta H^{\ddagger} + RT$. A temperature of 400 K, an intermediate value in the range over which the experimental activation energy was obtained (117−190 °C), was chosen for this purpose. In addition, computations involving larger basis sets were done in order to identify potential trends (see Table 2). Both the QCISD(T) and the MP4SDTQ calculations suggest a trend to a decreasing barrier as the basis set is expanded. This trend approaches the QCISD(T) results to the experimental value and leads to underestimated activation energies with MP4SDTQ. A further expansion of the basis set should therefore lead to a high consistency between QCISD(T) and experimental data. The situation is different with DFT calculations as the results provided by different basis sets vary over a more narrow range; also, they exhibit no clear-cut trend as the computational level is raised.

The electrocyclization barriers for (*E*)-dienimine and pentadienal are very similar and lower than those for hexatriene by 6−9 kcal/mol, depending on the particular computational method (see Table 1). This is consistent with the facts; thus, the experimental activation energy for (*E*)-dienimine is 17.5−22.5 kcal/mol[32] and that for pentadienal 21.7−22.4 kcal/mol.[32−34] It should be noted that the smallest decreases are those predicted by the QCISD(T) calculations; on the other hand, the B3LYP results reflect a much more marked decrease that leads to slightly better consistency with the experimental estimates. This assertion, however, should be taken cautiously owing to the low reliability of the experimental values, which were derived from dienimine and pentadienal analogues rather than from the compounds themselves. In any case, the electrocyclization of these heterosubstituted analogues of hexatriene appears to give rise to a substantial decrease in activation energy for the process. On the other hand, the electrocyclization of (*Z*)-dienimine raises the barrier by about 7 kcal/mol with the three computational methods tested. Although this cannot be experimentally confirmed, it will be of use in the subsequent comparisons.

The discussion that follows aims to interpret the calculated activation energies for the compounds studied. To complete and support this comparative analysis, the natural bond orbitals (NBOs) for each transition state were determined using MP2 and B3LYP electron densities.

From Table 3, which gives the Wiberg bond orders provided by the NBO calculations, and taking into account the differences in the bond orders, one can draw several interesting conclusions about the location of the transition state. Although the transition states of the four compounds are quite well "centered" in the reaction pathway, those for hexatriene, (*E*)-dienimine, and pentadienal are somewhat closer to the reactant, whereas that of (*Z*)-dienimine is closer to the product. This situation is accurately reproduced by the NBO calculations, which lead to three localized NBOs of the $\pi$ type in the $C_2-X_1$, $C_4-C_3$, and $C_6-C_5$ bonds for the first three compounds, whereas for (*Z*)-dienimine the calculations lead to two NBOs of $\pi$ type in the $C_3-C_2$ and $C_5-C_4$ bonds in addition to an NBO of preferentially p character (with a non-negligible s contribution) corresponding to the incipient $X_1-C_6$ bond. For this reason, the order of the $X_1-C_6$ bond in (*Z*)-dienimine is 0.423 with MP2 and 0.489 with B3LYP (see Table 3), both of which are substantially higher than the values for the other compounds. In the transition state, the new bond has formed to a considerably lesser extent in (*E*)-dienimine and pentadienal, with hexatriene in an intermediate position.

**Table 3. Wiberg Bond Orders Based on the Natural Atomic Orbitals (NAOs) Density Matrix for the Transition States as Calculated from MP2 and B3LYP Densities**[a]

| | hexatriene | (*E*)-dienimine | (*Z*)-dienimine | pentadienal |
|---|---|---|---|---|
| C2−X1 | 1.398 (1.476) | 1.526 (1.635) | 1.311 (1.412) | 1.412 (1.487) |
| C3−C2 | 1.309 (1.434) | 1.197 (1.285) | 1.361 (1.474) | 1.234 (1.339) |
| C4−C3 | 1.354 (1.423) | 1.406 (1.481) | 1.294 (1.367) | 1.349 (1.405) |
| C5−C4 | 1.309 (1.434) | 1.267 (1.373) | 1.384 (1.505) | 1.313 (1.425) |
| C6−C5 | 1.398 (1.476) | 1.425 (1.484) | 1.322 (1.405) | 1.388 (1.433) |
| X1−C6 | 0.349 (0.433) | 0.327 (0.382) | 0.423 (0.489) | 0.335 (0.382) |

[a] The B3LYP results are given in brackets.

In analyzing the nature of the incipient bond, one can compute natural localized molecular orbitals (NLMOs)[54] as a complementary task of the NBO routine.[48] NLMOs are similar to Boys or Edmiston−Ruedenberg localized molecular orbitals, but more efficiently calculated. Table 4 gives the bond orders[55,56] of the NLMOs corresponding to the interaction between atoms $X_1$ and $C_6$. These data reveal three distinct types of behavior. Thus, in hexatriene, the $X_1-C_6$ interaction is governed by the $C_5C_6$ and $C_1C_2$ $\pi$ molecular orbitals (+0.086) and, to a lesser extent, also by the $C_3C_4$ $\pi$ MO (+0.079). In (*E*)-dienimine and pentadienal, the greatest contribution to the interaction is clearly that of the lone pairs in the nitrogen and oxygen atom, respectively (the $C_1C_2$, $C_3C_4$, and $C_5C_6$ $\pi$ MOs contribute less markedly to it). The situation for (*Z*)-dienimine is rather different: as with NBOs, this configuration possesses an NLMO that exhibits an intrinsic $X_1-C_6$ interaction. Consequently, this MO provides the sole contribution to the bond order (+0.726), whereas the newly formed $C_2C_3$ and $C_4C_5$ MOs contribute by weakening the interaction (with −0.078 and −0.054, respectively).

In light of the previous results, it seems reasonable to assume a relationship between the three types of behavior derived from the NBO calculations and the three types of activation energies for the electrocyclization process. Therefore, the decreased barriers for (*E*)-dienimine and pentadienal must be closely related to the involvement

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**Table 4. Bond Orders of the Natural Localized Molecular Orbitals (NLMOs) for the Interaction between Atoms $X_1$ and $C_6$ in the Transition State**[a]

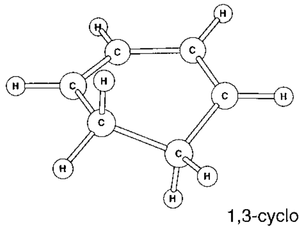
| | bond order | NLMO |
|---|---|---|
| hexatriene | +0.086 (+0.094) | $\pi$ (5−6) |
| | +0.086 (+0.094) | $\pi$ (1−2) |
| | +0.079 (+0.086) | $\pi$ (3−4) |
| (*E*)-dienimine | +0.083 (+0.098) | LP(1) |
| | +0.046 (+0.051) | $\pi$ (1−2) |
| | +0.040 (+0.039) | $\pi$ (3−4) |
| | +0.040 (+0.035) | $\pi$ (5−6) |
| (*Z*)-dienimine | +0.726 (+0.666) | (1−6)[b] |
| | −0.078 (−0.067) | $\pi$ (2−3) |
| | −0.054 (−0.026) | $\pi$ (4−5) |
| pentadienal | +0.094 (+0.103) | LP(1) |
| | +0.047 (+0.056) | $\pi$ (1−2) |
| | +0.037 (+0.035) | $\pi$ (3−4) |
| | +0.031 (+0.026) | $\pi$ (5−6) |

[a] The bond orders were calculated from the MP2 and B3LYP densities (B3LYP values are given in parenthese). Only the bond orders greater than 0.01 in magnitude are shown. [b] The hybrids that form this NLMO are of predominantly p character but also possess some s character (4.4% for $N_1$ and 7.8% for $C_6$ at the MP2 level and 4.5 and 7.3%, respectively, at the DFT level). In the MOs of pure $\pi$ character, the *s* character is virtually zero.

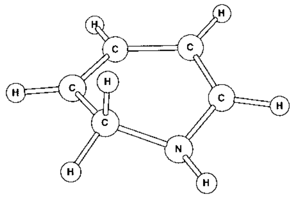
of a lone pair, which will facilitate the $X_1-C_6$ interaction by providing a reaction pathway with a lower energy expenditure. This involvement of a lone pair in the development of the new $\sigma$ bond has been shown to be one of the characteristic features of pseudopericyclic reactions;[57,58] however, other pseudopericyclic features such as planarity in transition states are not observed in the electrocyclizations studied. Although the nitrogen atom in (*Z*)-dienimine also possesses a lone pair, the geometric arrangement precludes its involvement in the bond formed. The imine hydrogen atom, which is inbound in the reactant, is a hindrance as it must rotate outward during the electrocyclization. This rotation motion undoubtedly hinders cyclization and can raise the activation energy as a result. Also, it may be related to a "delay" in the transition state as the $N_1{=}C_2$ must rotate slightly for the $N_1-C_6$ interaction to start. For this rotation to be feasible, the $N_1{=}C_2$ bond must lose much of its double character—at the transition state its bond order is only 1.311 whereas that of (*E*)-dienimine is 1.526 (see Table 3). The $C_3C_2N_1H$ dihedral in the transition state reaches 40.9° (MP2) or 44.8° (DFT) from 0.0° in the reactant.

It should be noted that, although the NBO calculations give slightly different results for the MP2 and DFT densities (see Tables 3 and 4), the previous discussion and its conclusions are applicable to both.

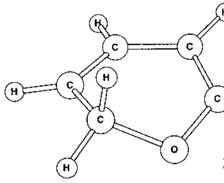
The involvement of the lone pair in the transition states of (*E*)-dienimine and pentadienal also results in marked geometric differences from the other two compounds. As can be seen from the right-hand column in Figure 3, in the transition state of hexatriene (with $C_s$ symmetry), the $C_5C_4C_3C_2$ and $C_2X_1C_6C_5$ dihedrals are completely planar. This conformation is also observed in (*Z*)-dienimine with relatively small deviations (5−18°) in the angles of these dihedrals. However, the geometry of the transition state in the other two compounds is rather different. Thus, deviations are much more marked, both in the $C_5C_4C_3C_2$ (19−25°) and especially in the $C_2X_1C_6C_5$ dihedral (30−42°). The substantial loss of planarity in the latter dihedral must be related to the need to adopt a geometric arrangement facilitating the interaction of the lone pair with $C_6$. By contrast, these two compounds exhibit a relatively planar zone in the $C_3C_2X_1C_6$ dihedral.



1,3-cyclohexadiene



1,2-dihydropyridine



2H-pyran

**Figure 4.** Structures of the cyclic forms as computed at the MP2 level. The B3LYP geometries are virtually identical, the sole difference being slight flattening of the ring.

Overall, the DFT and MP2 geometric results are similar. The greatest differences are of a few hundredths of an angstrom in bond distances and of 2−4° in bond and dihedral angles. Although these differences are substantially greater than those in the reactant geometries, they are still quite acceptable. In addition, they result in no appreciable effect or in any discrepancies in the conclusions reached.

**Closed Forms. Enthalpies of Reaction.** The three closed products of the electrocyclizations studied (viz. 1,3-cyclohexadiene, 1,2-dihydropyridine, and 2H-pyran) were optimized. Their structures are highly similar (see Figure 4, which shows their MP2 geometries). The three compounds—particularly 1,3-cyclohexadiene—exhibit two nearly planar zones (the $C_4C_3C_2X_1$ and $C_6C_5C_4C_3$ dihedrals) that result from the $C_2{=}C_3$ and $C_5{=}C_4$ double bonds. 1,3-cyclohexadiene (with $C_2$ symmetry) exhibits good consistency between its experimental[13,14] and calculated geometries (with both MP2 and B3LYP). Overall, the DFT results for the three products are very similar to their MP2 results in regard to bond lengths and angles. Although not especially significant, the greatest differences are those in the dihedral angles. This is the case with the three products but more prominent in 1,2-dihydropyridine and 2*H*-pyran than in 1,3-cyclohexadiene. In the former two, the B3LYP structure is slightly more planar than the MP2 structure; the greatest difference in this respect, however, is only about 13°.

Table 1 gives the energy difference between the reactants and their electrocyclization products (the rela-

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**Table 5. Computed Enthalpies of Reaction (in kcal/mol) at 298.15 K for the Studied Electrocyclations[a]**

| | QCISD(T) | MP4SDTQ | B3LYP |
|---|---|---|---|
| hexatriene | −16.6 | −17.3 | −13.2 |
| (*E*)-dienimine | −6.5 | −7.6 | −7.7 |
| (*Z*)-dienimine | −7.0 | −8.1 | −8.0 |
| pentadienal | 1.8 | 2.0 | 2.6 |

[a] The enthalpies were corrected for ZPE and thermal energies, using the MP2 or B3LYP scaled frequencies.

tive values given in brackets are all referred to the former). As can be seen, the hexatriene product is clearly more stable than the reactant, the energy difference ranging from 12.21 kcal/mol (B3LYP) to 16.27 kcal/mol (MP4SDTQ). The dienimine product is also more stable than the reactant, but the energy difference is much smaller than in hexatriene (5−7 kcal/mol). This trend results in pentadienal being more stable than its product with the three computational methods used. However, the energy difference between this reactant and its product is very small: from 2.76 kcal/mol with QCISD(T) to 3.44 kcal/mol with B3LYP. These small energy differences must be the reason for previous calculations being insufficient to conclusively confirm the higher stability of the reactant.[17,35−37]

By introducing thermal corrections, one can determine the enthalpy of reaction for each compound at a given temperature. Table 2 gives the enthalpy for the electrocyclization of hexatriene at 400 K as calculated at different computational levels. Although the experimental value is an estimate[27]—and must therefore be adopted cautiously—the MP4SDTQ and QCISD(T) methods appear to give accurate results whereas the B3LYP functional seemingly leads to underestimated $\Delta H$ values relative to their experimental counterpart. Moreover, the divergence appears to increase with increasing size of the basis set (the error exceeds 35% at the 6-311++G** level). Of all the calculations obtained in this work, this seems to be the only weakness of the DFT method relative to MP4SDTQ and QCISD(T). This, however, is not the case with all the compounds studied but only with hexatriene, as is clearly apparent from Table 5, which gives $\Delta H$ for all the electrocyclizations studied at 25 °C for comparison. Except for hexatriene, the three methods provide similar results, with negligible differences. Regarding the calculations at 0 K, introducing thermal effects always increases the stability of the product. The effect, however, is very modest (about 1 kcal/mol), so the previous conclusions still apply: the electrocyclization is a highly exothermic process for hexatriene, much less so for pentadienimine and slightly endothermic for pentadienal. This reveals a clear-cut, gradual tendency to instabilization of the closed forms relative to their open triene isomers when the terminal methylene groups are replaced with isoelectronic atoms.

## Conclusions

The present study has enabled a systematic comparison of the electrocyclization of hexatriene and its heterosubstituted derivatives. Calculations were extended to the whole process (reactants, transition structures, and products) and provided the results for quantities of a high interest such as activation energies and enthalpies of reaction.

The conformational analysis of the reactants suggests that the stability sequence and the geometry of the different conformers are essentially dictated by steric effects and hydrogen-bonding interactions. Thus, the *tZt* conformation is the most favored and also the only completely planar structure. However, the *tZc* and *cZt* conformations are only slightly more unstable. In addition, these latter are stabilized by a hydrogen-bonding interaction in (*E*)-dienimine and pentadienal. This interaction also results in planar conformations; specifically, in pentadienal, it brings conformer stabilities nearer (the *cZt* conformation is virtually isoenergetic or even very slightly more stable than the *tZt* conformation). In all the compounds studied, the *cZc* conformation, which is the precursor for the electrocyclization, is clearly the most unstable. This conformation is slightly less unfavored in (*E*)-dienimine and pentadienal owing to a hydrogen-bonding interaction that additionally increases structural planarity; such planarity, however, is only complete with DFT calculations. This is the sole divergence between the MP2 and DFT geometric results. As noted above, the discrepancy is seemingly negligible.

The calculated activation energies are quite consistent with the experimental estimates. The activation energies of (*E*)-dienimine and pentadienal are much lower than that of hexatriene (ca. 30 kcal/mol), and the opposite is true of (*Z*)-dienimine. The NBO results provide an explanation for these three types of behavior. The decreased electrocyclization barriers for (*E*)-dienimine and pentadienal appear to be the result of the involvement of a lone pair of the nitrogen or oxygen atom. In these two compounds, the contribution of the lone pair facilitates the interaction between atoms $X_1$ and $C_6$, thus favoring the formation of the new bond. In (*Z*)-dienimine, however, the configuration of the imine hydrogen atom hinders the contribution of the lone pair; also, the required rotation of the C=N bond imposes a further constraint on the electrocyclization. This appears to be the origin of the increased activation energy and “delayed” transition state—the only one among the four studied that is closer to the product than to the reactant.

Especially worth noting regarding the closed forms (the electrocyclization products) is their structural likeness. The calculated enthalpies of reaction exhibit a clear-cut trend arising from replacement of the methylene group with a nitrogen or oxygen atom. The electrocyclization of (*Z*)-hexa-1,3,5-triene to 1,3-cyclohexadiene is a definitely exothermic process; that of (*E*,*Z*)-[(2*Z*)-2,4-pentadienylidene]amine to 1,2-dihydropyridine is much less exothermic; and that of (2*Z*)-2,4-pentadienal to 2H-pyran is very slightly endothermic. The DFT method provides underestimated enthalpies, but only for hexatriene. This is the sole appreciable difference found in this work relative to the other computational methods used, which are much more expensive to implement.

**Acknowledgment.** I thank Roberto Rodríguez Fernández for his assistance as System Manager of the computer facilities used.

**Supporting Information Available:** Listings of (a) absolute electronic energies and ZPEs, (b) geometries of the most stable conformation for each reactant, (c) geometries of the transition structures, and (d) geometries of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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