Cooperative and Competitive Substituent Effects on the Cope Rearrangements of Phenyl-Substituted 1,5-Hexadienes Elucidated by Becke3LYP/6-31G* Calculations

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Abstract: B3LYP/6-31G* calculations have been performed on the Cope rearrangements of 1,5-hexadienes that are substituted with up to four phenyl groups. Experimental activation enthalpies are available for all of the compounds on which the calculations were performed, and the excellent agreement between the computed and the experimental values provides evidence that the calculated geometries of the transition structures and intermediates are reliable. The calculations confirm that, as suggested by the experimental data, phenyl substituent effects on the Cope rearrangement can be either cooperative or competitive. Based on the computed geometries of the transition structures, it is possible to explain why these two different types of substituent effects are observed.

The nature of the chair transition structure (TS) for the Cope rearrangement of 1,5-hexadiene has been the subject of numerous experimental and computational studies.[1] Multiconfigurational ab initio calculations that include dynamic electron correlation[2] and calculations based on density functional theory[3] concur that in the TS bond making and bond breaking are concerted and synchronous. However, as depicted in Figure 1, the TS contains contributions from the resonance structures for cyclohexane-1,4-diyl and for two allyl radicals; the contributions of each of these two different types of diradical structures are small at the TS geometry.[4] Therefore, the dominant contributor to the TS is the “aromatic” resonance structure in Figure 1, as has been confirmed by calculation of the diamagnetic susceptibility exaltation in the TS.[3b]

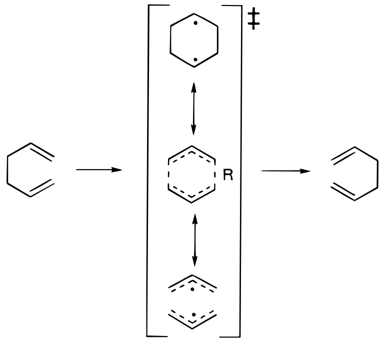

Figure 1. Schematic depiction of the bonding in the transition structure for the Cope rearrangement, showing the diradical resonance contributors (top and bottom) and the aromatic representation (center). *R* is the interallylic distance.

Although the nature of the TS for the Cope rearrangement of unsubstituted 1,5-hexadiene now seems well established,[2−4] a number of questions remain about the effects of radical stabilizing substituents on the TS. For example, how do radical-stabilizing substituents at different positions impact the contributions of the two diradical contributors to the electronic structure of the TS? Are substituent effects on the enthalpy of the TS additive? If not, are the substituent effects cooperative; or are they competitive? Does the geometry of the TS alter substantially in response to the number and placement of substituents?

Recent experimental studies by Doering and co-workers[5−7] have brought these important questions into sharp focus. Stimulated by Doering’s experimental results, we have carried out and reported the results of B3LYP/6-31G* calculations on the effects of cyano and vinyl substituents on the Cope rearrangement.[8] Unfortunately, the scant amount of experimental data for cyano[9] and vinyl[10] substituents has meant that most of these calculations were de facto done on model compounds, rather than on the phenyl-substituted 1,5-hexadienes for which

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the most complete set of experimental substituent effects has been reported.

Experiments have revealed that phenyl substituents at C-3,[11]C-1 and C-3,[5] C-1 and C-4,[12] or C-1, C-3, C-4, and C-6[7] of 1,5-hexadiene lower the activation enthalpy from that for the parent Cope rearrangement,[13] presumably by stabilizing the resonance contributor to the TS in Figure 1 that resembles two allyl radicals. Dewar and Wade found that phenyl substituents at C-2,[11] or C-2 and C-5[11,14] provide a larger enthalpy reduction per phenyl group. The lower enthalpy estimated for cyclohexane-1,4-diyl,[13,15] the resonance contributor to the TS that is stabilized by substituents at C-2 and C-5, relative to the enthalpy of two allyl radicals,[16] rationalizes this experimental finding.

A pair of phenyl substituents at C-2 and C-5[11,14] has been found to provide more than twice the lowering of the activation enthalpy than a single phenyl substituent at C-2.[11] Doering and co-workers have recently discovered that four phenyl groups attached to C-1, C-3, C-4, and C-6 of 1,5-hexadiene[7] also furnish more than twice the lowering of $\Delta H^{\ddagger}$ than is provided by a pair of phenyl groups at either C-1 and C-3[5] or C-1 and C-4.[12]

Experiments suggest that phenyl substituent effects can be competitive as well as cooperative. For example, when a pair of phenyl groups is attached to C-2 and C-4 of 1,5-hexadiene,[11] or when three phenyls are attached to C-1, C-3, and C-5,[5] small negative deviations from substituent effect additivity have been observed. A small negative deviation from additivity has also been found in the Cope rearrangement of 1,3-dicyano-2-phenyl-1,5-hexadiene.[6] Unfortunately, due to experimental uncertainties, especially in the value of $\Delta H^{\ddagger}$ for the Cope rearrangement of 2-phenyl-1,5-hexadiene,[11] these deviations from additivity are not outside the range of possible experimental errors.

A recent increase, by over an order of magnitude, in the computational resources available to us has made it possible to perform B3LYP/6-31G* calculations on the Cope rearrangements of 1,5-hexadienes that are substituted with up to four phenyl groups. Herein we report the results of these calculations. We find that our calculations give activation enthalpies that agree very well with the experimental values.[5−7,11−14] Consequently, there is good reason to believe that the information provided by our calculations about how phenyl substituents affect the TSs for these reactions is equally reliable.

Computational Methodology

Calculations were carried out with the 6-31G* basis set,[17] using Becke's hybrid exchange functional[18] and the nonlocal correlation functional of Lee, Yang, and Parr[19] (B3LYP). A vibrational analysis was performed at each stationary point found, to confirm its identity as an energy minimum or a transition structure. The harmonic frequencies were used, without scaling, to calculate the zero-point energies and thermal corrections necessary to obtain the enthalpies of reaction at 298 K. Optimized geometries, energies, and enthalpies of all the molecules discussed in this paper can be found as Supporting Information.

Table 1. Calculated and Experimental Activation Enthalpies (kcal/mol) for the Cope Rearrangements of Phenyl-Substituted 1,5-Hexadienes and the Calculated Interallylic Distance, *R* (Å), in Each TS and Intermediate

		$\Delta H^{\ddagger}$		
substituents	method	calcd	exptl	R^c
none	B3LYP	33.2	33.5 ± 0.5[13]	1.965
3-phenyl	B3LYP	28.4	28.1 ± 0.4[11]	2.122, 2.062
2-phenyl	B3LYP	30.4		1.837, 1.821
2-phenyl	UB3LYP	30.3		1.777, 1.700
2-phenyl	UB3LYP	29.4[a]	29.3 ± 1.6[11]	1.599
1-phenyl	B3LYP	36.2		2.062, 2.122
1,3-diphenyl	B3LYP	30.2	30.5 ± 0.2[5]	2.218
1,4-diphenyl	B3LYP	29.2	29.9 ± 0.2[12]	2.241
2,4-diphenyl	B3LYP	26.7	24.6 ± 0.8[11]	1.979, 1.900
2,4-diphenyl	UB3LYP	27.1[a,b]		1.597, 1.623
2,5-diphenyl	B3LYP	25.1		1.794, 1.680
2,5-diphenyl	UB3LYP	24.8		1.839, 1.667
2,5-diphenyl	UB3LYP	21.3[a]	21.3 ± 0.3[11,14]	1.576
1,3,5-triphenyl	B3LYP	29.2	27.8 ± 0.2[5]	2.113, 2.106
1,3,5-triphenyl	UB3LYP	32.7[a,b]		1.613
1,3,4,6-tetraphenyl	B3LYP	19.1	21.3 ± 0.1[7]	2.649

[a] Enthalpy, relative to the reactant, of the diradicaloid intermediate. [b] The UB3LYP TS, leading to this intermediate, was not located, because its enthalpy is clearly higher than that of the B3LYP TS. [c] Length of the forming bond and the breaking bond, respectively. A single bond length is given for those species having a plane of symmetry.

All electronic structure calculations were carried out with the Gaussian 98 suite of programs.[20] The program Quiver[21] was used for the calculations of secondary kinetic isotope effects.

Results and Discussion

For some of the Cope rearrangements with a phenyl substituent at C-2, unrestricted (U)B3LYP calculations found a cyclohexane-1,4-diyl intermediate of significantly lower energy than the B3LYP TS. For these reactions the UB3LYP TS connecting the intermediate to the reactant and product was also located. As shown in Table 1, in each case the enthalpies of the B3LYP and UB3LYP TSs were computed to be very similar.

Table 1 compares the computed with the measured values of $\Delta H^{\ddagger}$. In general, there is very good agreement between the two sets of values. The worst agreement is for the Cope rearrangement of 2,5-diphenyl-1,5-hexadiene. The B3LYP value of $\Delta H^{\ddagger}$ for a concerted Cope rearrangement and the UB3LYP value of $\Delta H^{\ddagger}$ for formation of a diradical intermediate in this reaction are each too high by nearly 4 kcal/mol. The UB3LYP TS has very little diradical character ($S^2 = 0.04$), compared to the diradical intermediate ($S^2 = 0.95$), to which the UB3LYP TS leads. The experimental enthalpy of the TS, relative to that of the reactant, is much closer to that of the UB3LYP intermediate than to those of either the B3LYP or UB3LYP TSs.

Does an Intermediate Really Exist in the Cope Rearrangement of 2,5-Diphenyl-1,5-hexadiene? To investigate

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whether, as indicated by the UB3LYP results, this reaction really is stepwise, with two unsymmetrical TSs flanking a symmetrical intermediate, or whether the reaction is concerted, with a symmetrical TS that resembles the UB3LYP intermediate, we calculated the secondary kinetic isotope effects (SKIEs) for both of these possibilities. One set of SKIE calculations was based on the pair of symmetry-related UB3LYP TSs, connecting the UB3LYP intermediate to the reactant and product. The other set of SKIE calculations was based on treating the C_{2h} UB3LYP intermediate as though it were the TS for the concerted Cope rearrangement of 2,5-diphenyl-1,5-hexadiene.

The SKIEs that we calculated for the Cope rearrangement of 2,5-diphenyl-1,5-hexadiene-d_4 at 55°—$k_H/k_D = 0.60$ for bond making and $k_H/k_D = 1.06$ for bond breaking—are in good agreement with the experimental values measured by Gajewski and Conrad.[22] However, the calculated values are essentially the same whether a single TS, with the same geometry as the UB3LYP intermediate, is assumed or whether this species is treated as a true intermediate, connected to the reactant and product by a pair of symmetry-related UB3LYP TSs. Therefore, comparison of the calculated and experimental isotope effects provides no information as to whether the geometry of the UB3LYP diradical intermediate or that of the UB3LYP TS is closer to the geometry of the actual TS for the Cope rearrangement of 2,5-diphenyl-1,5-hexadiene.

Very recently, Staroverov and Davidson have found that UDFT calculations, performed with the original Becke exchange functional (e.g., UBLYP), have a lower tendency to find diradical intermediates in Cope rearrangements than UDFT calculations, performed with Becke's hybrid exchange functional (e.g., UB3LYP).[23,24] Therefore, to investigate further whether a C_{2h} diradical intermediate really is formed in this reaction we also carried out UBLYP/6-31G* calculations on the Cope rearrangement of 2,5-diphenyl-1,5-hexadiene. The results of these calculations are described in detail in the Supporting Information, but they can be summarized as follows.

UBLYP/6-31G* calculations indicate that an intermediate is, indeed, formed in the Cope rearrangement of 2,5-diphenyl-1,5-hexadiene. However, UBLYP gives $S^2 = 0.00$ for this species, and the UBLYP energy for it is the same as that obtained from a (restricted) BLYP calculation. Therefore, with the BLYP functional, unlike the case with B3LYP, this intermediate can be described with a closed-shell wavefunction.

Comparison with experiment indicates that UB3LYP provides a much better estimate of the energy of this intermediate than (U)BLYP, probably because this intermediate really does have a large amount of diradical character. However, comparison with experiment also shows that UB3LYP overestimates the height of the barrier that separates the C_{2h} intermediate from the reactant. Presumably, because the TS that connects the reactant and the intermediate has less diradical character than the intermediate, UB3LYP is less successful in computing the energy of the TS than that of the intermediate.

Our BLYP (as well as our restricted B3LYP) calculations predict that the intermediate exists in a very shallow energy well. If this actually is the case, a good estimate of the enthalpy difference between the reactant and the TS that connects it to the intermediate should be provided by the UB3LYP enthalpy difference between the reactant and this intermediate. It is, presumably, for this reason that this UB3LYP enthalpy difference is closer than any of the computed values of the enthalpy of activation to the experimental value of $\Delta H^{\ddagger} = 21.3$ kcal/mol for the Cope rearrangement of 2,5-diphenyl-1,5-hexadiene.[11,14]

Cooperative and Competitive Substituent Effects. Our calculations predict that the two phenyl substituents in 2,5-diphenyl-1,5-hexadiene act cooperatively to lower the activation enthalpy for its Cope rearrangement and also the UB3LYP enthalpy of the putative diradical intermediate formed in this reaction. As shown in Table 1, substitution of a phenyl group at C-2 of 1,5-hexadiene is calculated to lower $\Delta H^{\ddagger}$ by ca. 3 kcal/mol and to give a diradicaloid intermediate whose UB3LYP energy is about 1 kcal/mol lower than either the B3LYP or UB3LYP TS. A second phenyl group at C-5 is calculated to lower $\Delta H^{\ddagger}$ by an additional 5 kcal/mol with both B3LYP and UB3LYP and to stabilize the UB3LYP diradical intermediate by an additional 8 kcal/mol, relative to the reactant. Thus, as found by comparing the experimental values of $\Delta H^{\ddagger}$ for the Cope rearrangements of 2-phenyl- and 2,5-diphenyl-1,5-hexadiene,[11,14] our calculations show that the effects of the two phenyl substituents in 2,5-diphenyl-1,5-hexadiene are non-additive and that these substituents act cooperatively.

Cooperative substituent effects on $\Delta H^{\ddagger}$ are also found by our calculations on Cope rearrangements in which phenyl groups are attached to the other four carbons—C-1, C-3, C-4, and C-6—of 1,5-hexadiene. This is not apparent if the value of $\Delta H^{\ddagger}$ for the Cope rearrangement of 3-phenyl-1,5-hexadiene to 1-phenyl-1,5-hexadiene is used, because the exothermicity of this reaction obscures the actual effect of the phenyl group in stabilizing the TS for this reaction.[25] However, a value for this stabilization can be obtained by using Marcus theory.[26]

The Marcus equation predicts that, in the absence of additional TS stabilization by the phenyl substituent in the Cope rearrangement of 3-phenyl-1,5-hexadiene, the average value of $\Delta H^{\ddagger}$ for the forward and the reverse reactions would be approximately equal to the intrinsic barrier for the Cope rearrangement.[27] An average value of $\Delta H^{\ddagger} = 32.3$ kcal/mol is computed for the Cope rearrangements of 1-phenyl- and 3-phenyl-1,5-hexadiene. This value is ca. 1 kcal/mol lower than $\Delta H^{\ddagger}$ for the parent reaction. We take this difference as a reasonable estimate of the stabilization, not present in the reactant or product, of the Cope TS by a single phenyl group at C-1 or C-3 of 1,5-hexadiene.

The Cope rearrangements of 1,3- and 1,4-diphenyl-1,5-hexadiene are degenerate; hence, their activation enthalpies can be compared directly with that for the unsubstituted parent. The two phenyl groups on the same allyl fragment in the former compound are calculated to be slightly less effective in lowering

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[24] For example, UB3LYP/6-31G* calculations on the potential energy surface for the parent Cope rearrangement predict the existence of a C_{2h} diradicaloid ($S^2 = 0.63$) intermediate, albeit one that is 3.2 kcal/mol higher in energy than the C_{2h} aromatic TS.[8,23] In contrast, UBLYP/6-31G* calculations, like CASSCF calculations to which dynamic electron correlation has been added,[1e,2] do not find a C_{2h} diradical intermediate on the potential energy surface for this reaction.[23]

[25] The exothermicity of 7.8 kcal/mol that is computed for this reaction by our B3LYP/6-31G* calculations is 2.7 kcal/mol higher than the value recommended by Doering for the conjugation energy in *trans-β*-alkylstyrenes.[5] RHF and MP2/6-31G* calculations give enthalpies of, respectively, $\Delta H = -6.4$ and -3.3 kcal/mol for the rearrangement of 3-phenyl- to 1-phenyl-1,5-hexadiene, and it appears that B3LYP generally does tend to overestimate conjugation energies between double bonds and other unsaturated groups.[8]

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[27] The Marcus equation actually predicts that the average activation enthalpy should be raised by the square of the exothermicity, divided by 16 times the intrinsic barrier, but this quotient amounts to only 0.1 kcal/mol.

$\Delta H^\ddagger$ ($\Delta\Delta H^\ddagger = 3.0$ kcal/mol) than the phenyl group on each allyl fragment in the latter ($\Delta\Delta H^\ddagger = 4.0$ kcal/mol). The selective stabilization of the Cope TS by the second phenyl group in 1,3- or 1,4-diphenyl-1,5-hexadiene is 2−3 kcal/mol more than the ca. 1 kcal/mol provided by a single phenyl substituent at just one of these carbons.

The two additional phenyl substituents in 1,3,4,6-tetraphenyl-1,5-hexadiene have an even larger cooperative effect on $\Delta H^\ddagger$. The four phenyl groups in this compound are computed to lower $\Delta H^\ddagger$ by a total of 14 kcal/mol. Thus, the second pair of phenyl groups provides an additional 10−11 kcal/mol of selective stabilization of the TS, roughly a factor of 4 more than the first pair of phenyl substituents.

In agreement with experiment, our calculations predict that a phenyl group which stabilizes one of the resonance structures shown in Figure 1 causes additional phenyl substituents at equivalent positions in the TS to have an even larger stabilizing effect. However, although our calculations show that phenyl substituents attached to equivalent carbons in the Cope TS act cooperatively to lower $\Delta H^\ddagger$, our calculations also predict that competitive effects occur when phenyl substituents stabilize different diradical contributors to the Cope TS.

For example, based on a computed value of $\Delta H^\ddagger = 30.2$ kcal/mol for the Cope rearrangement of 1,3-diphenyl-1,5-hexadiene, and $\Delta\Delta H^\ddagger = 2.8$ kcal/mol calculated for the effect of the phenyl group in 2-phenyl-1,5-hexadiene, substituent effect additivity predicts $\Delta H^\ddagger = 27.4$ kcal/mol for the Cope rearrangement of 1,3,5-triphenyl-1,5-hexadiene. However, the B3LYP enthalpy of activation, $\Delta H^\ddagger = 29.2$ kcal/mol, indicates a negative deviation of 1.8 kcal/mol from substituent effect additivity.

A deviation from additivity of about this size is also found in the experimental value of $\Delta H^\ddagger$,[5] but this deviation is within the range of experimental error. The computational results in Table 1 provide evidence that the observed deviation is real.[28]

TS Geometries. What is responsible for the cooperative and competitive substituent effects, predicted by our B3LYP calculations and observed experimentally? We believe that the answer is given by B3LYP TS geometries, which are shown in Figure 2.

The interallylic bond lengths in the (U)B3LYP TSs, which are listed in Table 1 and shown in Figure 2, change dramatically with the number and placement of phenyl substituents. For example, a 2-phenyl substituent causes the average of the forming and breaking single bonds in the B3LYP TS to be 0.14 Å shorter than in the parent Cope rearrangement, while a second phenyl, attached at C-5, causes a 0.09 Å further contraction. A 3-phenyl substituent causes an average of 0.13 Å increase in forming and breaking single bond lengths in the B3LYP TS, but in the 1,3,4,6-tetraphenyl TS these lengths are longer than in the TS for the parent Cope rearrangement by 0.17 Å per phenyl group, for a total increase of 0.68 Å!

The bond orders of the forming and breaking single bonds in the parent Cope TS are 0.49,[29] reflecting a synchronous, concerted reaction. For substituted cases, these bond lengths in the TS or intermediate range from 1.576 to 2.649 Å. These correspond to bond orders ranging from 0.94 to 0.06! The secondary kinetic isotope effects measured by Gajewski and Conrad[24] provide strong experimental evidence for a variable TS, whose geometry responds to the positions of radical stabilizing substituents in the TS.[30]

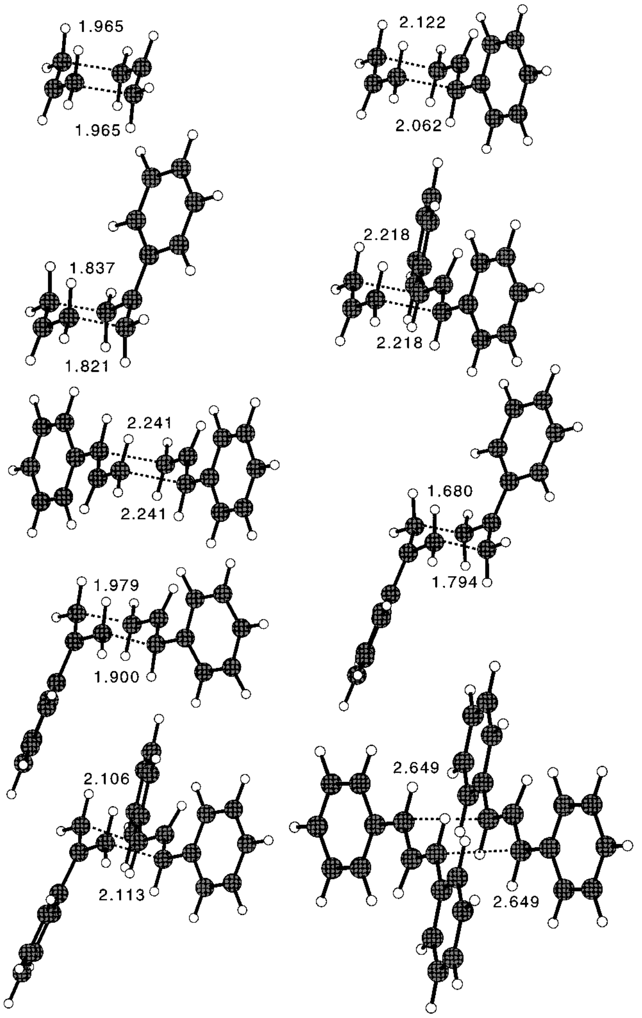

Figure 2. Geometries of the B3LYP transition structures for the parent and phenyl-substituted Cope rearrangements.

The overlay in Figure 3 compares the geometries of the 1,4- and 2,5-diphenyl-substituted, chair, Cope TSs. In addition to the obvious difference between interallylic bond lengths, this figure also reveals graphically the difference between the amount of pyramidalization at the terminal atoms of the allyl fragments in the two TSs.

In the B3LYP TS for Cope rearrangement of 1,4-diphenyl-1,5-hexadiene (shown in gold), the pyramidalization angles[31] are 21.7° at the phenyl-substituted carbons and 21.6° at the unsubstituted carbons. Figure 3 shows that in this TS the phenyl groups are conjugated with the atomic orbitals that form the bonds that are being made and broken. However, even at an interallylic distance of 2.241 Å, bonding between the two allyl fragments keeps the phenyl-substituted carbons from being any more planar than the unsubstituted carbons at the allyl terminii.

In the UB3LYP TS for Cope rearrangement of 2,5-diphenyl-1,5-hexadiene (shown in silver) the larger amount of bonding between the two allylic fragments makes the terminal carbons much more pyramidal than in the TS for Cope rearrangement

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[28] Since B3LYP/6-31G* calculations predict $\Delta H^\ddagger = 29.7$ kcal/mol for the Cope rearrangement of 1,3-dicyano-1,5-hexadiene,[8] if substituent effects were additive, $\Delta H^\ddagger = 26.9$ kcal/mol would be expected for the Cope rearrangement of 1,3-dicyano-2-phenyl-1,5-hexadiene. Our B3LYP/6-31G* calculations actually give $\Delta H^\ddagger = 28.5$ kcal/mol for this reaction. The calculated negative deviation of 1.6 kcal/mol from additivity is slightly smaller than the 2.2 kcal/mol negative deviation found experimentally.[6]

[29] The Indiana/Pauling bond order relationship is used: $n_p = e^{(R_o - R)/0.6}$: Houk, K. N.; Gustafson, S. M.; Black, K. A. *J. Am. Chem. Soc.* **1992**, *114*, 8565. For a discussion of TS bond lengths in pericyclic reactions, see ref 1c.

[30] Gajewski, J. J. *Acc. Chem. Res.* **1980**, *13*, 142.

[31] These are the angles between the bonds to C-2 and the planes formed by the terminal carbons and the two substituents attached to them.

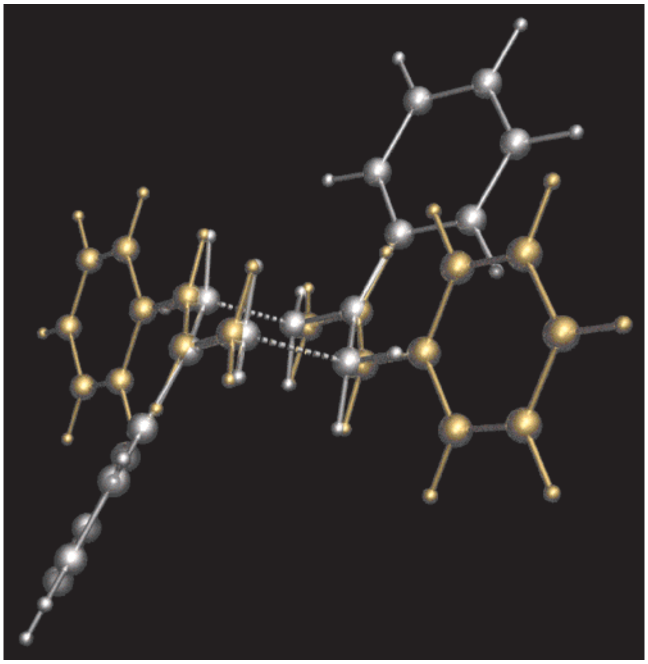

Figure 3. Superposition of the transition structures for the Cope rearrangements of 1,4-diphenyl-1,5-hexadiene (gold) and 2,5-diphenyl-1,5-hexadiene (silver); B3LYP geometry for the former and UB3LYP for the latter.

of 1,4-diphenyl-1,5-hexadiene. In the 2,5-diphenyl TS, the pyramidalization angles[31] are 36.2° and 46.4° at the terminal carbons where the interallyic distances are, respectively, 1.839 and 1.667 Å.

As shown in Figure 3, the phenyl groups attached to C-2 and C-5 are twisted slightly out of conjugation in the TS (as they are in the reactant) by the steric interaction between one of the *ortho* hydrogens in each phenyl substituent and the *cis* hydrogen at the more planar of the pair of adjacent carbons. As a result, the pyramidalization angle at C-2 and C-5 of 18.8° in the TS for Cope rearrangement of 2,5-diphenyl-1,5-hexadiene is larger than that of 12.7° in the TS for Cope rearrangement of 1,4-diphenyl-1,5-hexadiene.

However, in the UB3LYP diradical intermediate in this reaction, the phenyl groups are aligned to conjugate maximally with the radical centers at these two carbons. The increased conjugation flattens C-2 and C-5, so that the pyramidalization angle decreases from 18.8° in the UB3LYP TS to 7.0° in the intermediate. The change in phenyl conformation between the TS and the intermediate is noteworthy, since phenyl conformation has been invoked as a possible factor in antibody catalysis of the Cope rearrangement of a 2,5-diphenyl-1,5-hexadiene.[32]

Effect of TS Geometry on Cooperativity. The differences in TS geometries, revealed by our calculations and shown graphically in Figures 2 and 3, reflect alterations in the weights of one of the two diradical contributors to the TS.[8,33] Multiple phenyl substituents at the same types of carbons in the Cope TS favor more diradical-like TS geometries, thus allowing each substituent to provide more stabilization for the TS than it can when fewer phenyl substituents are present. Therefore, it is the changes in the TS geometries, caused by multiple substituents, that lead to the cooperative substituent effects, calculated for and observed in the Cope rearrangements of 2,5-diphenyl-1,5-hexadiene[11,14] and 1,3,4,6-tetraphenyl-1,5-hexadiene.[7]

In contrast, when substituents are attached to different types of carbons in the TS, they stabilize different diradical contributors to it. The optimal TS geometry is then a compromise. This explains why, for example, the average value of R in the Cope TS for 1,3,5-triphenyl-1,5-hexadiene is 0.108 Å shorter than R in the Cope TS for 1,3-diphenyl-1,5-hexadiene.

At such a compromise TS geometry neither set of substituents can provide as much stabilization as it can at the TS geometry in which the set of competing substituents is absent. This explains why $\Delta H^{\ddagger}$ for the Cope rearrangement of 1,3,5-triphenyl-1,5-hexadiene is higher than would be expected if the effects of the phenyl groups in 1,3-diphenyl- and 2-phenyl-1,5-hexadiene were additive.

Conclusions

The results of (U)B3LYP/6-31G* calculations on the effects of phenyl substituents on the Cope rearrangement show the same type of excellent agreement with experiment, previously found in B3LYP/6-31G* calculations of $\Delta H^{\ddagger}$ for the Cope rearrangements of 1,5-hexadiene,[3] more highly unsaturated derivatives,[34] and semibullvalene.[35] This agreement with experiment, regarding the effect of phenyl substituents on $\Delta H^{\ddagger}$, provides evidence that the TS geometries obtained from our calculations are equally reliable.

The calculated TS geometries provide the explanation of why both cooperative and competitive phenyl substituent effects are observed in Cope rearrangements. Multiple phenyl groups, attached at the same types of carbons in the TS, all stabilize the same diradical contributors to the TS, leading to a more diradical-like TS geometry. At such a geometry each phenyl substituent can provide more stabilization for the TS than it can when fewer phenyl groups are present.

In contrast, phenyl substituents attached to different types of carbons in the Cope TS stabilize each of the possible diradical contributors to it. The optimal TS geometry is then a compromise. At such a geometry neither set of phenyl substituents can provide as much stabilization as it can at the more diradical-like TS geometry that is favored when the competing set of phenyl substituents is absent.

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Supporting Information Available: Optimized geometries and energies for the reactants, TSs, and intermediates in Table 1, and detailed discussion of the results of UBLYP calculations on the existence of a C_{2h} intermediate in the Cope rearrangement of 2,5-diphenyl-1,5-hexadiene (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) Driggers, E. M.; Cho, H. S.; Liu, C. W.; Katzka, C. P.; Braisted, A. C.; Ulrich, H. D.; Wemmer, D. E.; Schultz, P. G. *J. Am. Chem. Soc.* **1998**, *120*, 1945. Ulrich, H. D.; Mundroff, E.; Santarsiero, B. D.; Driggers, E. M.; Stevens, R. C.; Schultz, P. G. *Nature* **1997**, *389*, 271.

(33) Staroverov and Davidson have shown that at fixed geometries the weights of the two diradical contributors to the Cope TS are less affected by the addition of cyano substituents than by changes in the geometry of the TS, caused by these substituents.[23]

(34) Black, K. A.; Wilsey, S.; Houk, K. N. *J. Am. Chem Soc.* **1998**, *120*, 5622.

(35) Jiao, H.; Nagelkerke, R.; Kurtz, H. A.; Williams, R. V.; Borden, W. T.; Schleyer, P. von R. *J. Am. Chem Soc.* **1997**, *119*, 5921.