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Theoretical Study of the Diels−Alder Reaction of Selenoaldehydes and Selenoketones

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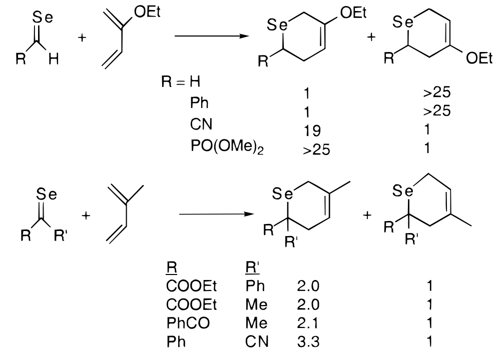
The Diels−Alder reaction of a series of substituted selenoaldehydes (Se═CHR; R = H, F, Me, OMe, CH_2F, CF_3, and CN) or selenoketones (Se═CR_2; R = Me and CN) with 1,3-butadiene or 2-methoxy-1,3-butadiene to yield 3,6-dihydro-2*H*-selenopyrans were examined using B3LYP with a modified 6-31G* basis set. This method is compared with results from a number of standard ab initio procedures and compares well with post-HF results. The Diels−Alder reaction of the selenocarbonyl compounds proceeds through a concerted, though asynchronous, transition state. Strong electron-withdrawing groups alter the mechanism; a charge-transfer complex is first formed, followed by a concerted TS before reaching the heterocyclic product. The transition state geometry, regiochemistry, and dependence of the activation barrier on substituents can be understood in terms of FMO theory.

Introduction

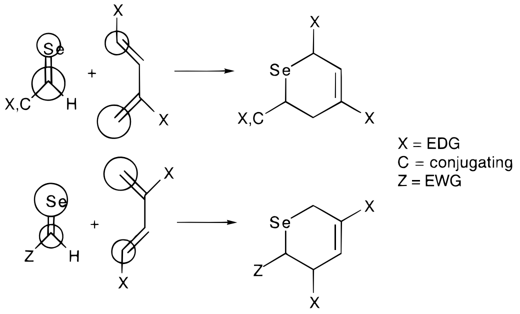
Diels−Alder (DA) cyclizations play an important role in the synthesis of heterocyclic molecules, providing a unique opportunity for regio- and stereocontrol.[1] Until recently, DA reactions of chalcogen-substituted dienes or dienophiles were limited to the oxygen family. The thio- and selenocarbonyl compounds are quite reactive toward dimer- and oligomerization. Preparation of thiocarbonyl compounds is often carried in situ with a diene for their immediate trapping.[2]

In the mid-1980s Kirby[3] and Krafft and Meinke[4−9] developed methods to synthesize selonaldehydes and selenoketones. These were reacted in situ with an activated diene to yield the DA adduct. Krafft and Meinke[4−9] extensively explored the chemistry of these selenocompounds. The regioselectivity was found to correlate with substituent attached to the carbonyl of the selenoadehyde or selenoketone (see Scheme 1).

Scheme 1



Scheme 2



This regiochemistry can be explained in terms of simple FMO arguments. The reaction is dominated by the $LUMO_{dienophile}−HOMO_{diene}$ interaction. Meinke and Krafft[8] proposed the simple model sketched in Scheme 2 to predict the regiochemistry. Similar chemistry and FMO arguments have been drawn for the thiocarbonyl compounds. Further, they find a strong *endo* selectivity in reactions of selenoaldehydes with cyclopentadiene.

Wilker and Erker examined the reaction of aryl selenoketones with *trans,trans*- and *cis,trans*-2,4-hexadiene.[10] The DA reaction with the *trans,trans* isomer led to the *cis* product (retention of stereochemistry) only, indicative of the standard concerted pericyclic mechanism. How-

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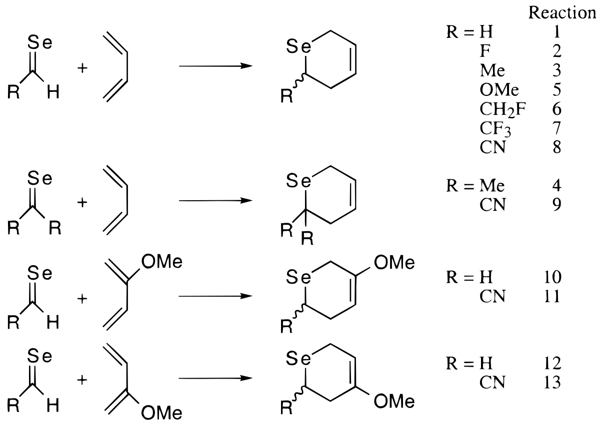
Scheme 3



ever, reaction of the *cis,trans* isomer with either seleno- or thioketones also gave the *cis* product (here the *inversion* product). They suggest that steric congestion in the reaction of the *cis,trans* isomer leads to a diradical intermediate, which after rotation about a C–C bond can revert to the *trans,trans* isomer. While their study is not conclusive on the nature of the reaction mechanism, with uncongested dienes there is strong evidence to suggest a concerted reaction.

We have long been interested in pericyclic reactions of heterosystems.[11–20] In this paper, we report a theoretical examination of the Diels–Alder reaction of a series of substituted C=Se systems. We find that substituent effects conform to the standard FMO model. With strong electron-withdrawing groups, the mechanism is complicated by a charge-transfer intermediate. The DA reaction of selenoaldehydes and selenoketones overall follows a concerted, though asynchronous, path regardless of substituent.

Computational Method

The Diels–Alder reaction of 1,3-butadiene or 2-methoxy-1,3-butadiene and a variety of selenoaldehydes and selenoketones shown in Scheme 3 were examined. These substituted selenocarbonyl compounds span a range of donating and withdrawing strengths, enabling us to explore systematic trends for comparison with experimental results.

Reactions of all of the selenoaldehydes except selenoformaldehyde can proceed through an *exo* or *endo* transition state leading to psuedoaxial or psuedoequatorial substitution on the ring. We will use a simple naming convention for the transition states: **TS*No*** where ***N*** is the reaction number and ***o*** is the orientation **x** for *exo* or **n** for *endo*. Similarly, the products will be labeled **P*No***.

Table 1. Activation and Reaction Energies (kcal mol^{-1}) for Reaction 1

method	E_a	E_{rxn}
HF/6-31G*MOD	18.72	−45.81
MP2/6-31G*MOD	1.37	−48.73
MP4SDTQ/6-31G*MOD//MP2/6-31G*MOD	5.45	−43.93
B3LYP/6-31G*MOD	2.83	−44.54

All calculations were performed using GAUSSIAN-94.[21] The basis set used throughout this study is formed by using the 6-31G* set for all first-row atoms and H and the contracted 641(d) basis set[22] for Se. We will refer to this basis set as 6-31G*MOD.

We have used the B3LYP[23] method for obtaining molecular geometries, energies, and electron distributions. While this choice has obvious practical advantages (conventional ab initio methods would be far too slow to complete this study), we were concerned whether this approach would provide reasonable results. Over the past few years, a number of investigations of the adequacy of the DFT procedure for predicting energetics of Diels–Alder reactions have appeared. Jursic and Zdravkovski[24] and Wiest, Montiel, and Houk[25] have examined the parent Diels–Alder reaction (ethylene + 1,3-butadiene) and find that the B3LYP method provides barrier and reaction energies within a few kcal mol^{-1} of experiment, which is comparable to MP4 and QCISD results. Barone and Arnaud[26] examined the Diels–Alder reaction of 1,3-butadiene with ethylene, formaldehyde, and thioformaldehyde, the two analogous compounds to the parent we are interested in here (selenoformaldehyde). The B3LYP barrier lies between the MP2 and QCISD(T) results, with nice agreement between the DFT and QCISD(T) barriers and reaction energies.

Since no evaluation of computational method for selenocarbonyl systems are available, we examined reaction 1 (1,3-butadiene + selenoformaldehyde) at a variety of levels (Table 1). As is typically found for Diels–Alder reactions, the HF barrier is too large and the MP2 barrier is too low.[11,27] The B3LYP and MP4SDTQ barriers differ by only 1.62 kcal mol^{-1} and the reaction energies are within about a half a kcal mol^{-1}. In a previous study, we found the B3LYP method to provide geometries of a number of organoselenium compounds in close agreement with experiment, and superior to the HF and MP2 geometries.[28] Therefore, we believe the B3LYP method is suitable for evaluating the Diels–Alder reactions of selenocarbonyl compounds. All energies reported in this work were obtained at the B3LYP/6-31G*MOD//B3LYP/

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6-31G*MOD level and corrected for zero-point vibrational energy (also obtained at this level and scaled by 0.98[29]). We did not explictly search for stepwise reactions nor intermediates, except where specifically discussed below. Nevertheless, there is ample precedence within the literature that these types of Diels–Alder reactions are likely to proceed preferentially through a concerted pathway.[25,30]

Bond orders were obtained by using eq 1, an empirical relationship based on the value of the electron density at the bond critical point, $\rho(r_c)$. The values of $\rho(r_c)$ were determined using the routines in GAUSSIAN-94.

$$\mathrm{BO(X-Y)} = \exp[A(\rho(r_c) - B)] \qquad (1)$$

X–Y	A	B
C–C[31]	6.458	0.252
C–Se[28]	15.37	0.148

Results

Geometries. The optimized geometries of the products of reactions 1–13 are drawn in Figure 1. All of the calculated structures of these 3,6-dihydro-2*H*-selenopyrans are in similar half-chair conformations. The geometric parameters about the ring are very similar, regardless of substitution. Methoxy substitution at C_4 or C_5 (**P10–13**) has little effect on the ring geometry.

Substitution on C_2 has a slightly greater effect. In the unsubstituted compound (**P1**) the C_2-C_3 distance is 1.527 Å. Substitution of any kind (except F) increases this distance, the extreme case being the dicyano analogue (**P9**) where $r(C_2-C_3) = 1.552$ Å. The $Se-C_2$ distance also varies with C_2 substitution. While all substituents lengthen this bond, the longest are for the methoxy compounds **P5x** and **P5n**, though the $Se-C_2$ distance in the dicyano compound is almost as long. The methoxy substituent result suggests perhaps an anomeric effect, but the C–O distances do not reflect this, and the variation in the $Se-C_2$ length is much less than what is seen on the pyrans or thiopyrans.[20] Since all of the substituents lead to longer bonds, it is easiest to rationalize the effect as simply due to steric interactions.

The optimized geometries of the transition structures for reactions 1–13 are drawn in Figure 2. The bond distances within the forming ring are summarized in Table 2. A number of trends appear with these data. The range of the C–C distances for each bond within the diene fragment is fairly narrow; in fact, the entire range is only from 1.354 to 1.438 Å. This narrow range suggests that these bond changes are concerted and synchronous and relatively insensitive to substituent. The range for the $Se-C_2$ distance is also small; the longest distance is in **TS5n**.

While these distances show little substituent effect, the same is decidedly not true for the forming $C_2\cdots C_3$ and $Se\cdots C_6$ bonds. The distance between C_2 and C_3 ranges from 2.947 Å in **TS9** to 2.190 Å in **TS5n**, a range more than 1 order of magnitude greater than for the ranges of the bonds within the two fragments. The average distance is about 2.4 Å, a bit longer than typical for Diels–Alder reactions.[30b] This is also noted in Diels–Alder transition states involving P and S in the π-system. The C_2-C_3 distance is longer in the *exo* orientation than in the *endo* form. There is a strong correlation between the type of substituent attached to selenocarbonyl carbon and the C_2-C_3 distance—electron-donating groups shorten the distance while electron-withdrawing groups lengthen the distance.

The range of the $Se-C_6$ distance is also very wide. In this case, however, F, Me, OMe, and CH_2F substituents make small changes on the distance, with the distance always shorter in the *exo* conformation. Cyano and CF_3 (in the *exo* position) cause a significant shortening of the $Se-C_6$ distance in the TSs. Interestingly, **TS9** has the longest C_2-C_3 distance and the shortest $Se-C_6$ distance.

Last, methoxy substitution on C_2 of butadiene has a strong effect on the forming bond distances. In comparing **TS1** with **TS10** and **TS12**, the methoxy group leads to a shorter C_2-C_3 distance while it shortens the $Se-C_6$ distance in **TS10** and greatly lengthens it in **TS12** (it is the longest $Se-C_6$ distance). The same relative trend is also seen for reactions 11 and 13 when compared to reaction 8.

Energies. The B3LYP/6-31G*MOD activation and reaction energies for all 13 reactions are listed in Table 3. As discussed in Computational Methods, this procedure provides reasonable energetics, certainly such that trends will be reliable.

All of the reactions are exothermic, ranging from about −30 to −40 kcal mol^{-1} except for reaction 5, which is much less exothermic (−21 kcal mol^{-1}). The difference between the *endo* and *exo* product is quite small, all less than 1 kcal mol^{-1} except for reaction 2 (*endo* favored by 1.01 kcal mol^{-1}) and reaction 3 (*exo* favored by 1.22 kcal mol^{-1}).

The activation energy for reaction 1 is only 4.89 kcal mol^{-1}. This is substantially lower that for the prototype Diels–Alder reaction of 1,3-butadiene with ethylene (21.36 kcal mol^{-1} at B3LYP/6-31G*[26]). It is also smaller than the activation energies for the Diels–Alder reaction of butadiene with formaldehyde (21.10 kcal mol^{-1}) or thioformaldehyde (6.50 kcal mol^{-1}).[26]

The substituents cause a systematic change in the activation energy. Electron-donating groups increase the activation energy (reaction 2–5) while electron-withdrawing groups decrease the barrier (reactions 6–9). In fact, the barrier for reaction 9 is *negative*, which indicates that an intermediate must be present along the reaction path. This will be discussed further in a later section.

For most of the reactions, there is little kinetic preference for the *endo* or *exo* pathway. The differences in the conformational TSs is less than 1 kcal mol^{-1}, and there is no trend in which pathway is preferred. The exception is reaction 6 where the *endo* path is preferred by 3.44 kcal mol^{-1}.

Bond Orders. The bond orders for the ring bonds in the TSs are listed in Table 4. These bond orders are obtained using the empirical formula given in eq 1 which is based on the electron density. We have found this type of analysis of use in judging the extent of reaction at the TS. There is greater variation in the bond orders of the diene and dienophile fragment than what we have seen in other Diels–Alder reactions. Often these bond orders

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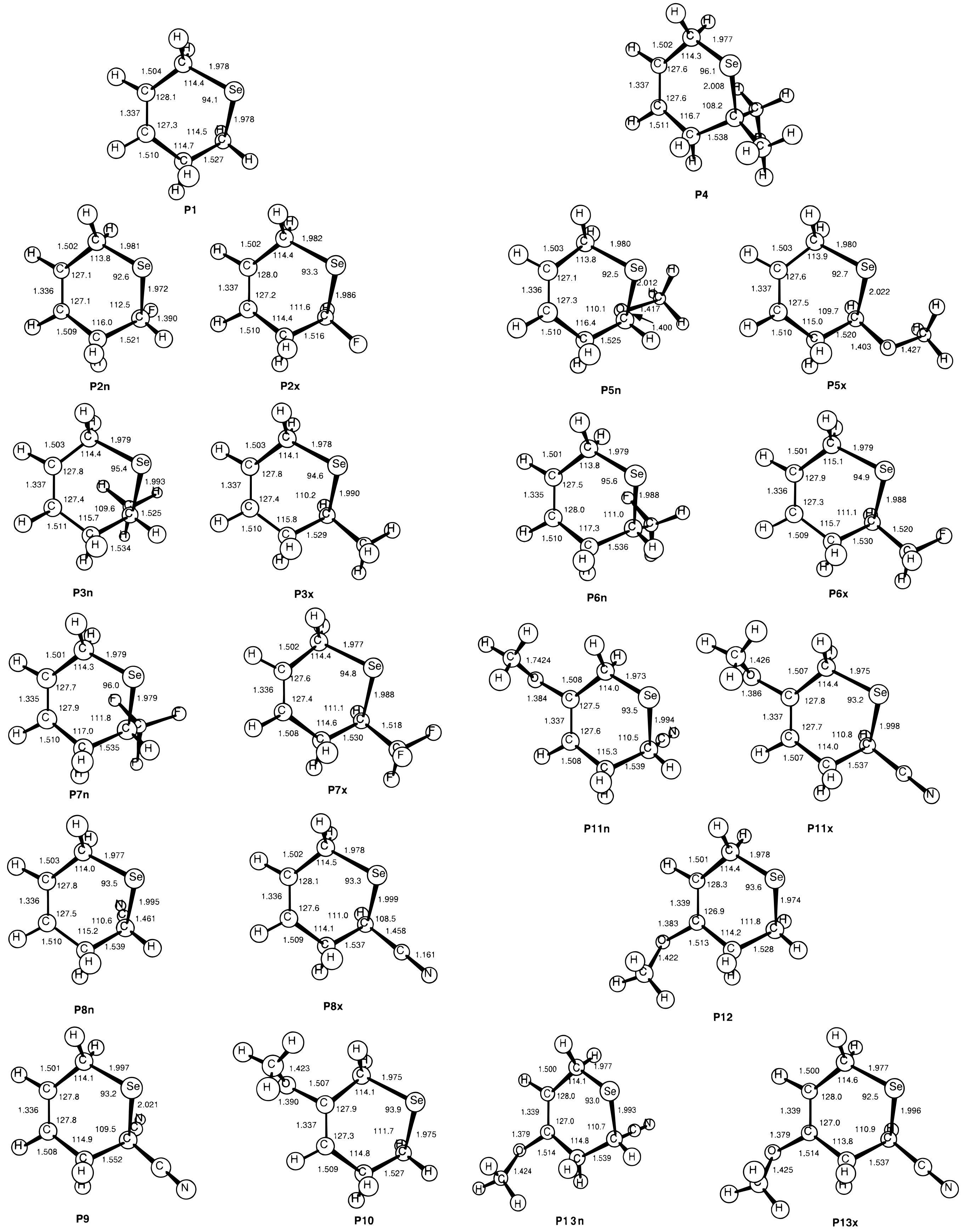

Figure 1. B3LYP/6-31G*MOD-optimized geometries of the products of reactions 1−13. All distances are in angstroms, and all angles are in degrees.

are quite similar within a given TS, suggesting a synchronous reaction. These selenium Diels−Alder reactions, however, appear to be asynchronous; in the parent reaction, the bond orders within the diene and dienophile

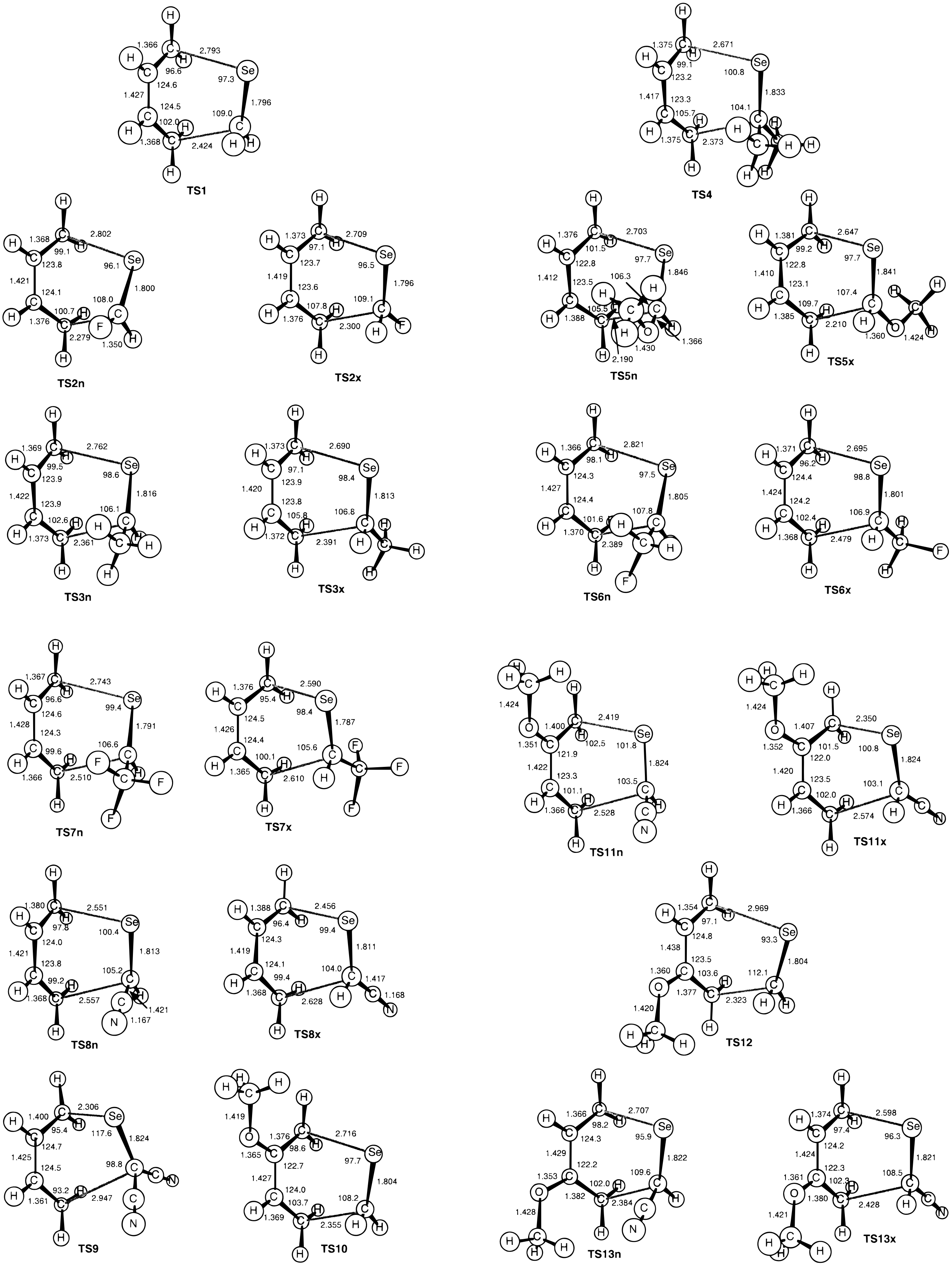

Figure 2. B3LYP/6-31G*MOD-optimized geometries of the transition structures for reactions 1−13. All distances are in angstroms, and all angles are in degrees.

Table 2. Atom Distances in TS1−TS13

	forming bonds		diene			dienophile
	$C_2\cdots C_3$	$Se\cdots C_6$	$C_3\cdots C_4$	$C_4\cdots C_5$	$C_5\cdots C_6$	$Se\cdots C_2$
TS1	2.424	2.793	1.368	1.427	1.366	1.796
TS2n	2.279	2.802	1.367	1.421	1.368	1.800
TS2x	2.300	2.709	1.376	1.419	1.373	1.796
TS3n	2.361	2.762	1.373	1.422	1.369	1.816
TS3x	2.391	2.690	1.372	1.420	1.373	1.813
TS4	2.373	2.671	1.375	1.417	1.375	1.833
TS5n	2.190	2.703	1.388	1.412	1.376	1.846
TS5x	2.210	2.647	1.385	1.410	1.381	1.841
TS6n	2.389	2.821	1.370	1.427	1.366	1.805
TS6x	2.479	2.695	1.368	1.424	1.371	1.801
TS7n	2.510	2.743	1.366	1.428	1.367	1.791
TS7x	2.610	2.590	1.365	1.426	1.376	1.787
TS8n	2.557	2.551	1.368	1.421	1.380	1.813
TS8x	2.628	2.456	1.368	1.419	1.388	1.811
TS9	2.947	2.306	1.361	1.425	1.400	1.824
TS10	2.355	2.716	1.369	1.427	1.376	1.804
TS11n	2.528	2.419	1.366	1.422	1.400	1.824
TS11x	2.574	2.350	1.366	1.420	1.407	1.824
TS12	2.323	2.969	1.377	1.438	1.354	1.804
TS13n	2.384	2.707	1.382	1.429	1.366	1.822
TS13x	2.428	2.598	1.380	1.424	1.374	1.821

Table 3. Activation and Reaction Energies (kcal mol^{-1}) for Reactions 1−13

reaction	E_a	E_{rxn}	reaction	E_a	E_{rxn}
1	4.89	−39.42	7*exo*	1.15	−41.69
2*endo*	9.29	−33.04	8*endo*	2.08	−36.84
2*exo*	8.89	−32.03	8*exo*	1.22	−36.58
3*endo*	9.26	−32.43	9	−4.01	−33.41
3*exo*	9.85	−33.65	10	7.13	−33.92
4	14.33	−28.04	11*endo*	2.83	−30.99
5*endo*	16.99	−21.05	11*exo*	1.88	−30.89
5*exo*	17.52	−20.88	12	5.94	−34.43
6*endo*	4.72	−35.55	13*endo*	2.63	−31.25
6*exo*	8.16	−35.88	13*exo*	3.38	−31.34
7*endo*	1.90	−41.70			

Table 4. Bond Orders in TS1−13 Using Eq 1

	forming bonds		diene			dienophile	
	$C\cdots C$	$C\cdots Se$	C_3-C_4	C_4-C_5	C_5-C_6	$Se-C_2$	total
TS1	0.290	0.164	1.696	1.489	1.784	1.569	6.992
TS2n	0.312	0.154	1.669	1.489	1.806	1.582	7.012
TS2x	0.304	0.167	1.677	1.513	1.765	1.636	7.062
TS3n	0.294	0.167	1.675	1.502	1.770	1.514	6.922
TS3x	0.289	0.172	1.687	1.512	1.760	1.531	6.951
TS4	0.291	0.173	1.672	1.520	1.752	1.457	6.865
TS5n	0.322	0.173	1.614	1.539	1.735	1.361	6.744
TS5x	0.334	0.181	1.629	1.554	1.715	1.387	6.780
TS6n	0.294	0.159	1.690	1.483	1.794	1.516	6.936
TS6x	0.280	0.175	1.703	1.507	1.759	1.631	7.055
TS7n	0.279	0.168	1.712	1.490	1.783	1.633	7.065
TS7x	0.268	0.189	1.732	1.508	1.736	1.703	7.136
TS8n	0.270	0.192	1.715	1.519	1.724	1.607	7.026
TS8x	0.261	0.213	1.730	1.526	1.691	1.647	7.068
TS9	0.231	0.388	1.802	1.527	1.534	1.616	7.098
TS10	0.296	0.178	1.678	1.564	1.774	1.595	7.085
TS11n	0.254	0.276	1.698	1.429	1.714	1.623	6.994
TS11x	0.254	0.274	1.755	1.562	1.609	1.674	7.128
TS12	0.250	0.162	1.769	1.557	1.579	1.686	7.003
TS13n	0.303	0.136	1.643	1.436	1.909	1.376	6.803
TS13x	0.304	0.140	1.656	1.461	1.886	1.372	6.819

fragments of the TS are 1.70 1.49, 1.78, and 1.57, clearly spanning a good range.

On the other hand, the sum of the active bond orders for most of the reaction is very close to 7, the value one would associate with a concerted reaction. We have typically found a sum indicative of concert for hetero-Diels−Alder reactions.[14,20,32] The only outlier is reaction 5, and here the sum is off by only 0.25, not a large amount considering the extrapolations involved in the fitting procedure.

Discussion

The purpose of this study is 3-fold: to evaluate the appropriateness of the DFT method, to understand the reaction mechanism, and to determine the applicability of FMO theory to selenium systems. We begin with the evaluation of the B3LYP/6-31G*MOD method.

The method evaluation shown in Table 1 establishes that high-level conventional ab initio methodology (which has been successful in modeling many DA reactions) and B3LYP calculations for reaction 1 are in close agreement on the activation and reaction energy. While this is very encouraging, comparison of calculated energies with experiment would be more satisfying. While there are no thermodynamic measurements of selenium-DA reactions, the experiments in the first part of Scheme 1 indicate a strong regiochemical substituent effect.[6,8] We calculated the energetics of reactions 10−13 to compare with these experimental results.

The reaction of selenoaldehyde with 2-methoxy-1,3-butadiene can give the meta product (reaction 10) or the para product (reaction 12). The barrier for the latter pathway is 1.19 kcal mol^{-1} lower, and the para product is also lower in energy (0.44 kcal mol^{-1}) than the meta. Simple Arrhenius rates, assuming identical *A* factors, would predict a 7.5:1 para-to-meta ratio, in reasonable agreement with the experiment, where only the para product is observed. In comparing reactions 11 and 13, the meta product is kinetically favored by 0.75 kcal mol^{-1}. It is also the thermodynamic product, though only by 0.36 kcal mol^{-1}. The experiment indicates the meta product is produced in a 19-fold excess over the para product, and simple Arrhenius kinetics predict a 3.5-fold excess of the meta product. These results certainly support the contention that the B3LYP method is suitable for analyzing hetero-substituted DA reactions.

Examination of the geometries and bond orders of the transition structures clearly indicates a concerted reaction. While we did not explicitly search for intermediates or nonconcerted TSs, the TS searches were unconstrained and could have located such a structure. It is important to keep in mind two considerations in this regard. First, computational examination of the DA reaction (including heteroatoms) strongly indicate a concerted TS.[25,30] Second, Wilker and Erker's[10] experiments support a concerted TS when steric congestion is minimal. Further studies of this point are underway in our laboratory, but for all of the reactions examined here, there is little congestion and a concerted pathway is certainly anticipated and consistent with all previous experience.

We next discuss the dienophile substituent effect. Using the parent reaction (reaction 1) as a reference, systematic substitution effects can be clearly observed. Reactions 2−5 involve an EDG on the dienophile. For these reactions, the forming C_2-C_3 and $Se-C_6$ distances are generally shorter than in **TS1**; the shortest occur in reaction 5 where the substituent (MeO) is the strongest donor. The $Se-C_2$ distance in these TSs are longer than in **TS1**. The bond orders generally follow this pattern as

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(32) (a) Bachrach, S. M.; Perriott, L. M. *Can. J. Chem.* **1996**, *74*, 839. (b) Salzner, U.; Bachrach, S. M. *J. Organomet. Chem.* **1997**, *529*, 15−22.

Table 5. HOMO and LUMO Energies (hartrees) of the Dienes and Dieonophiles

	R_1, R_2	HOMO	LUMO
dienophiles	H, OMe	−0.320	0.087
$Se{=}CR_1R_2$	Me, Me	−0.309	0.065
	H, Me	−0.317	0.058
	H, F	−0.349	0.052
	H, H	−0.326	0.044
	H, CH_2F	−0.334	0.014
	H, CN	−0.365	−0.014
	CN, CN	−0.398	−0.059
dienes	1,3-butadiene	−0.331	0.139
	2-methoxy-1,3-butadiene	−0.320	0.145

well. The distances and bond order trends suggest that as the substituent becomes a stronger donor, the TS is later.

The Hammond postulate correlates TS position with reaction energy; the more endothermic a reaction is, the later the TS. Reaction energy increases (i.e., less exothermic) in the order reaction 1 < 2 < 3 < 4 < 5. This correlates completely with the increasingly later TS implied by the distances and bond orders. The activation energies also correlate with the substituent type—as the donor becomes stronger, the barrier increases.

If these trends continue with the EWG (reactions 6−9), one would expect an earlier TS, greater exothermicity, and lower barriers with increasing EWG strength. Some of these trends are observed. The forming C_2-C_3 distance in the TSs increases with stronger EWG; it is very long in **TS9**. However, the $Se-C_6$ distances are short in the TS for reactions 7−9. The bond order mimics these distances. While reaction 7 is the most exothermic of the reactions examined, reactions 6, 8, and 9 are less exothermic than the parent reaction. Interestingly (and most importantly), the activation barrier *does* decrease with increased EWG strength.

The relationship of substituent with activation barrier can be readily understood in terms of traditional FMO theory. A decreasing barrier with increasing withdrawing strength implies a DA reaction that is governed by the normal-demand $HOMO_{diene}-LUMO_{dienophile}$ frontier orbital interaction. Inspection of Table 5, which lists the HOMO and LUMO energies for the selenocompounds (dienophiles) and the dienes, finds that this is the dominant orbital interaction. Further, the smaller this gap, the smaller the activation barrier.

The trend observed concerning the relative distances of the forming bonds can also be interpreted using FMO theory. When the dienophile has an EDG, the C_2-C_3 distance is shorter than the $Se-C_6$ distance, but this reverses when an EWG is attached to the dienophile. The LUMO of the dienophile with an EDG has a dominant coefficient on C, indicating a preference to form new bonds to this atom. On the other hand, the LUMO of the dienophile with an EWG will have diminished differences in the coefficients on C and Se, perhaps even with a dominant Se coefficient. This would suggest initial preference toward forming the bond to Se.

FMO theory can also be used to explain the regiochemistry of reactions 10−13. Since these seleno-DA reactions have normal electron demand, the orbital coefficients of the HOMO of the diene and LUMO of the dienophile are needed. We obtain these coefficients using NBO analysis.[33] In the HOMO of 2-methoxy-1,3-butadiene, the coefficient on C_1 is larger than on C_4. For selenoformaldehyde, the C and Se coefficients in the LUMO are −0.758 and 0.652, respectively. FMO theory thus predicts the major product to be the para product, in line with experiment and the DFT calculations. For the cyano-

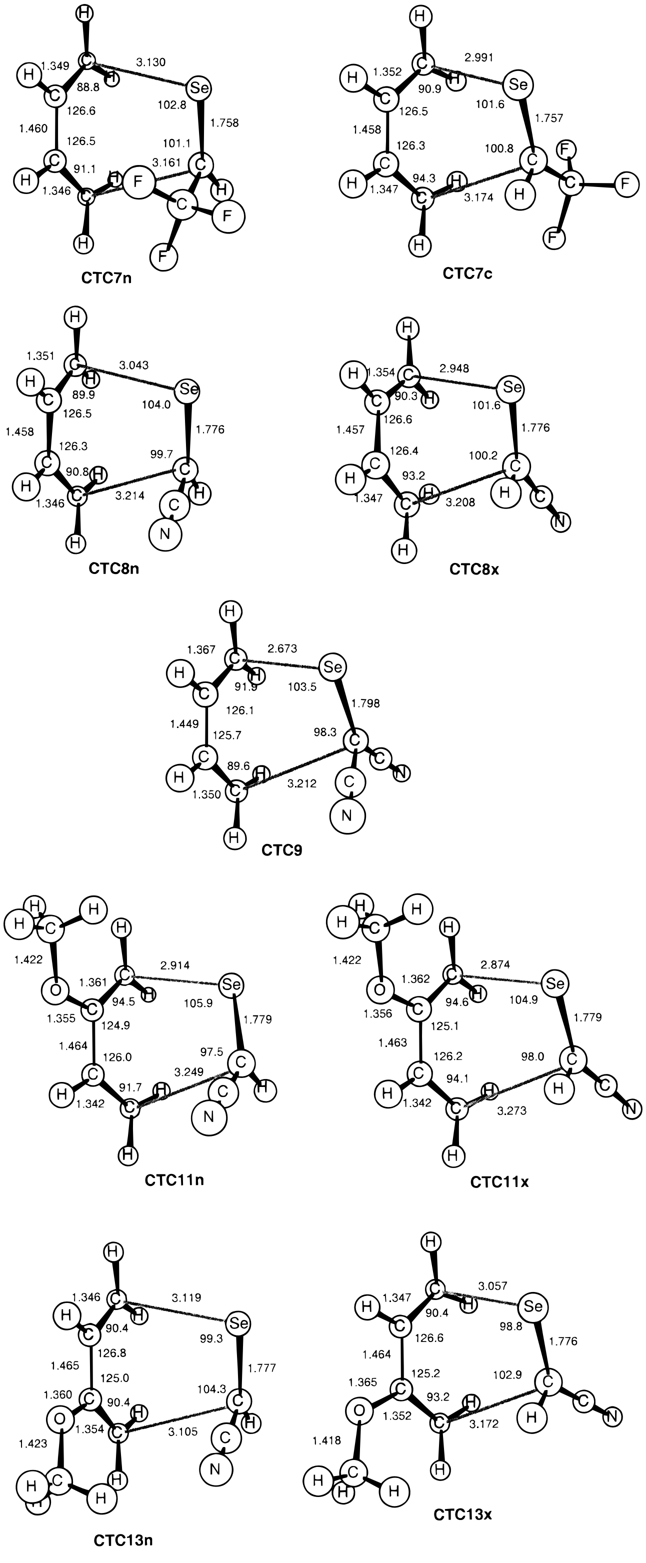

Figure 3. B3LYP/6-31G*MOD-optimized geometries of the charge-transfer complexes. All distances are in angstroms, and all angles are in degrees.

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(33) a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Weinhold, F.; Curtiss, L. A.; Pochatko, D. J. *J. Chem. Phys.* **1986**, *84*, 5687−5705.

Table 6. Relative Energies (kcal mol^{-1}) of the CTC Intermediates[a]

	E_{rel}		E_{rel}
CTC7n	−0.07	**CTC11n**	−0.80
CTC7x	−0.61	**CTC11x**	−1.35
CTC8n	−0.53	**CTC13n**	−0.42
CTC8x	−0.89	**CTC13x**	−0.07
CTC9	−4.22		

[a] Energy relative to reactants, calculated at B3LYP/6-31G*MOD+ZPE.

substituted selenoaldehyde, the C and Se coefficients are −0.724 and 0.689, respectively. This too would suggest the para product, which is not observed, but notice that the changes in the coefficients are in the correct direction. This model is consistent with the one proposed by Krafft and Meinke.[8]

While these seleno-DA reactions are concerted, they are not synchronous. Examination of the distances (Table 2) and bond orders (Table 4) within the TSs clearly indicate that the bonds are not breaking and forming to the same extent within a TS. The forming double bond between C_4 and C_5 trails the breaking of the two π bonds within the diene fragment. For most of the reactions, the C_2-C_3 bond is better formed in the TS than the $Se-C_6$ bond.

TS9 is the real outlier of the group in many regards. Its C_2-C_3 distance is extremely long while having a very short $Se-C_6$ distance. Perhaps most eye-catching is the negative activation energy for reaction 9. A negative activation energy is a clear indication that the chosen reactants are not directly connected to this TS. An intrinsic reaction coordinate (IRC) search starting from **TS9** and proceeding in the reverse direction located a local energy minimum that is more stable than the isolated reactants. In fact, such a complex was located for all reactions involving a strong electron-withdrawing group (CF_3 or CN; reactions 7, 8, 11, and 13). These complexes are labeled **CTC*No*** in a manner similar to the TSs. (The designation **CTC** stands for charge-transfer complex as discussed below.) These complexes are drawn in Figure 3. The structures of these complexes possess a cyclic arrangement reminiscent of the TSs except with much longer distances separating the two fragments.

The relative energies of these complexes are listed in Table 6. All of these complexes are more stable than isolated reactants, though by a small amount except for **CTC9**. What is most striking is that **CTC9** is more than 4 kcal mol^{-1} more stable than the reactants. Using **CTC9** as the starting point for the DA reaction, the barrier actually is +0.21 kcal mol^{-1}, very small but positive.

What is the reason for these stable complexes? A few experimental studies of the Diels–Alder reactions of tetracyanoethylene and anthracene have suggested a charge-transfer complex lies along the reaction path.[34] Since the LUMO of the selenocarbonyl is quite low, and is further lowered by an EWG, perhaps these complexes involve charge transfer from the diene to the selenocarbonyl fragment. NBO[33] analysis of these complexes gives the atomic charge on each atom. The sum of the atomic charges of the atoms of the diene fragment are listed in Table 7. Electrons are shifted from the diene to the dienophile, and these species are stabilized by the electrostatic interaction of the fragments. For the most stable complex, **CTC9**, almost a full quarter of an electron is transferred, due to the very low-lying LUMO of the dienophile (see Table 5). Therefore, the reaction of a diene with an electron-deficient selenocarbonyl compound first gives a charge-transfer complex. The complex then continues on to the heterocycle through a concerted TS. Reactions with other selenocarbonyl compounds appears to react via a concerted, single-step DA reaction.

Table 7. Charge Transfer from Diene to Dienophile in the Charge-Transfer Complexes[a]

	charge transfer (*e*)		charge transfer (*e*)
CTC7	−0.10	**CTC9**	−0.24
CTC8	−0.13	**CTC11**, **CTC13**	−0.14

[a] Charge transfer obtained by summing the NBO atomic charges for each fragment.

Conclusion

This study reports the first application of density functional theory to a pericyclic reaction involving selenium. The B3LYP method appears to provide very reasonable geometries and energies for this type of reaction, certainly suitable for comparisons within a series of substituted species.

The Diels–Alder reactions of simple selenocarbonyl compounds with sterically uncongested dienes proceed via a concerted, though asynchronous, TS. Frontier molecular orbital theory can be employed to predict the regiochemistry and the substituent effects on activation energy. Last, when the selenocarbonyl has strong electron-withdrawing groups attached, the Diels–Alder reaction proceeds through an intermediate charge-transfer complex. Unfortunately, the barrier from this complex to the heterocycle product is small, making detection of the complex difficult.

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