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Diels−Alder Reactions of Cyclopentadiene and 9,10-Dimethylanthracene with Cyanoalkenes: The Performance of Density Functional Theory and Hartree−Fock Calculations for the Prediction of Substituent Effects[†]

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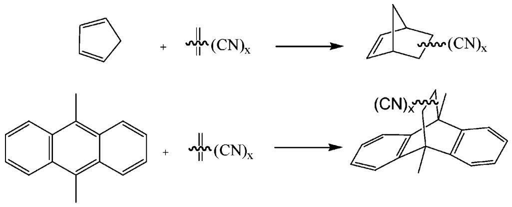
The activation enthalpies for the reactions of cyclopentadiene with ethylene, acrylonitrile, fumaronitrile, maleonitrile, vinylidene cyanide, tricyanoethylene, and tetracyanoethylene have been computed with the Hartree−Fock quantum mechanical method and a variety of density functionals (B3LYP, BPW91, and MPW1K) and compared to classic experimental data obtained by Sauer, Wiest, and Mielert (*Chem. Ber.* **1964**, *97*, 3183). Some significant errors in B3LYP activation enthalpies involving cyano groups, especially 3 or 4 cyano groups, have been identified, whereas HF and MPW1K reproduce substituent effects quite accurately.

Introduction

In 1964, Sauer, Wiest, and Mielert published a now-classic kinetic study of Diels−Alder reactions.[1] The study quantified the enormous effect of cyano substituents on rates of cycloaddition of two typical dienes, cyclopentadiene and 9,10-dimethylanthracene, with all of the cyano-substituted ethylenes from acrylonitrile (cyanoethylene) through tetracyanoethylene (TCNE).



At 20 °C, the rates of TCNE cycloadditions with cyclopentadiene and 9,10-dimethylanthracene are faster than cycloadditions of acrylonitrile by 10^7 and 10^{10} times, respectively. The rates of cycloaddition of cyclopentadiene with TCNE and ethylene differ by 10^{12}, corresponding to a 17 kcal/mol lowering of activation energy by tetracyano substitution.

Over the four decades since that publication, a variety of theoretical treatments have explored substituent effects on cycloaddition rates,[2−9] and the Sauer data have served as the most dramatic effect example of pure electronic effects on rates that are not complicated by significant steric effects.

In connection with our benchmarking studies of theoretical methods for the computation of activation energies,[10] we were struck by the apparent inability of the B3LYP density functional method, a normally robust method, to reproduce these well-known substituent effects.

Here, we report calculations on Diels−Alder cycloadditions of cyclopentadiene with cyanoethylenes using Hartree−Fock theory and density functional theory with the B3LYP, BPW91, and MPW1K functionals, each of which has been advocated as a good and practical method to study pericyclic reactions. Diels−Alder reactions of 9,10-dimethylanthracene with acrylonitrile and TCNE were also studied with the HF and MPW1K methods. We have also studied charge-transfer complexes of tetracyanoethylene with cyclopentadiene, anthracene, and 9,-10-dimethylanthracene using HF, B3LYP, and MPW1K methods. Our aims are to evaluate which of the methods provide a good correlation with experimental rates and to gain more insight into mechanistic details of these prototypical Diels−Alder reactions.

Background. Sauer et al. carried out a systematic study of the rates of Diels−Alder reactions of cyclopentadiene and 9, 10-dimethylanthracene with the series of cyanoalkenes from acrylonitrile (cyanoethylene) through TCNE (tetracyanoethylene) in dioxane at 20 °C.[1] These data are summarized in Tables 1 and 2 along with other experimental data.

The values for the activation barriers given in Table 1 were estimated using $\Delta\Delta H^{\ddagger} = -RT \ln(k_1/k_2)$ from TS theory, assuming a constant activation entropy. Rate constants were taken from Sauer's kinetic studies.

Each cyano group increases the rate of reaction, and there is a dramatic increase in the rate for the unsymmetrically substituted dienophile, 1,1-dicyanoethylene. Tetracyanoethylene reacts 10 million times faster than cyanoethylene (approximately 1 s versus 1 decade!).

In the case of the Diels−Alder reactions of 9,10-dimethylanthracene with cyanoethylenes (Table 2), the rates of reaction of *cis*- and *trans*-1,2-dicyanoethylene proceed at about at the same rate as reactions with cyclopentadiene. The reactivity of tetracyanoethylene with 9,10-dimethylanthracene is 100 times

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TABLE 1: Experimental Relative Rates and Estimated Activation Enthalpies for Diels−Alder Reactions between Ethylene, Cyanoethylenes, and Cyclopentadiene[a]

ethylene substituent	$10^5 \cdot k$ ($M^{-1}s^{-1}$)	$\Delta H^{\ddagger}$
none	8.3×10^{-4}[c]	22.5[c]
CN	1.04[b]	15.5[d]
trans-1,2-$(CN)_2$	8.06×10^{1}[b]	12.8[d]
cis-1,2-$(CN)_2$	9.10×10^{1}[b]	12.8[d]
1,1-$(CN)_2$	4.55×10^{4}[b]	9.0[d]
1,1,2-$(CN)_3$	4.8×10^{5}[b]	7.6[d]
1,1,2,2-$(CN)_4$	4.30×10^{7}[b]	5.0[d]

[a] Energies are in kcal/mol. [b] Dioxane, 293 K, see ref 1. [c] Gas phase, 521−570 K, see Walsh, R.; Wells, J. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 52. [d] Estimated from relative rates with the equation $\Delta\Delta H^{\ddagger} = -RT \ln k_1/k_2$.

TABLE 2: Experimental Relative Rates and Estimated Activation Enthalpies for Diels−Alder Reactions of 9,10-Dimethylanthracene with a Series of Cyanoethylenes

	$10^5 \cdot k$ ($M^{-1}s^{-1}$)	E_a	$\Delta H^{\ddagger}$
CN	0.89[a]	15.8[a]	15.0[a]
trans-1,2-$(CN)_2$	1.31×10^{2}[a]	12.3[a]	11.6[a]
cis-1,2-$(CN)_2$	1.39×10^{2}[a]	12.4[a]	11.8[a]
1,1-$(CN)_2$	1.27×10^{5}[a]		8.0[b]
1,1,2-$(CN)_3$	5.9×10^{6}[a]		5.7[b]
1,1,2,2-$(CN)_4$	1.3×10^{10}[a]	−1.5[c] 4.4[d] 2.9[d] 1.7[d] −1.9[d]	1.2[b]

[a] Dioxane, 293 K, ref 1. [b] Estimated from $\Delta\Delta H^{\ddagger} = -RT \ln k_1/k_2$, which assumes $\Delta\Delta S^{\ddagger} = 0$ eu. [c] CCl_4, 298 K, ref 19. [d] Top to bottom: *o*-xylene, toluene, benzene, (all at temperatures ranging from 286 to 313 K) and dichloromethane (285 to 298 K); ref 12.

TABLE 3: Activation Barriers from Experimental Studies and Previous Computational Studies of Diels−Alder Reactions of Cyclopentadiene with Cyanoethylenes at 298 K, Except Where Indicated

	HF	AM1[d]	B3LYP	BP	BLYP	MP2	MP3	$\Delta H^{\ddagger}_{exptl}$[i]
CN	26.0[a] 35.9[b] 36.1[c]	29.9 30.4	16.4[d] 18.0[e] 21.2[e] 17.5[f]	9.8[g]	15.2[g]	5.4[h] 6.7[g]	18.5[g]	15.5
trans- 1,2-$(CN)_2$			15.2[f]					12.8
cis- 1,2-$(CN)_2$			16.3[f]					12.8
1,1-$(CN)_2$		28.7	9.3[d] 12.3[e] 15.7[e] 10.5[f]					9.0
1,1,2-$(CN)_3$			11.3[f]					7.6
1,1,2,2-$(CN)_4$			11.5[f]					5.0

[a] 3-21G, ref 3. [b] 6-31G(d), ref 5. [c] 6-31G//3-21G, ref 5. [d] Reference 6. [e] /6-31G(d)//AM1, /6-311G(2d,2p)//AM1, in order, ref 6. [f] Reference 9 (computed at 293 K). [g] Reference 7. [h] Reference 5. [i] 293K, estimated from the $\Delta\Delta H^{\ddagger}$for reaction of cyclopentadiene with ethylene, see Table 1.

greater than that of cyclopentadiene, whereas cyanoethylene reacts faster with cyclopentadiene than with 9,10-dimethylanthracene.

Several groups have determined the activation enthalpy of the Diels−Alder reaction of 9,10-dimethylanthracene with tetracyanoethylene. Lotfi and co-workers have determined the activation barrier to be −1.5 kcal/mol in CCl_4 at 25 °C,[11] indicative of the intervention of a charge-transfer complex. Kiselev and Miller have investigated solvent effects on the activation barrier[12] with activation barriers ranging from −2.43 ($CHCl_3$) to 4.38 (*o*-xylene). Negative activation barriers were observed in nonaromatic and slightly polar solvents.

Previous Computational Studies. Previous theoretical and computational studies for Diels−Alder reaction of cyclopentadiene with cyanoethylenes are summarized in Table 3.

Houk and Munchausen reported ionization potentials of several cyanoalkenes and discussed the relationship of these to Diels−Alder reactivities.[2] The fact that cyclopentadiene is more reactive than 9,10-dimethylanthracene with acrylonitrile but the opposite reactivity order is observed with tetracyanoethylene was rationalized by frontier molecular orbital theory. Houk and Jorgensen et al. also studied Diels−Alder reactions of cyclopentadiene with acrylonitrile using MP2, HF/3-21G and AM1 methods.[3] It was shown that AM1 and HF overestimate the activation barrier by more than 10 kcal/mol, but all agreed on the concerted, but asynchronous, nature of the reaction.

Sustmann and Sauer et al. have explored the observed endo selectivities of [4+2] cycloadditions of cyanoethylenes and have noted the role of solvent effects on these selectivities.[4] Jorgensen et al. studied the reaction of cyclopentadiene with several dienophiles, including acrylonitrile, using HF, MP2, and MP3 methods. MP2 underestimates the activation barrier for the cycloaddition reaction between cyclopentadiene and acrylonitrile, whereas HF overestimates it. MP3 gives better results but is very time-consuming.[5] Jursic studied the cycloadditions of cyclopentadiene with acrylonitrile and 1,1-dicyanoethylene using the AM1 and B3LYP methods.[6]

Branchadell explored the reactions of cyclopentadiene with acrylonitrile, ethylene, and acrolein using a variety of methods including density functionals BP, BLYP, and B3LYP.[7] It was found that BLYP and B3LYP give activation barriers in good agreement with experimental data. MP2 underestimates activation barriers by 9 kcal/mol, whereas HF overestimates the barriers. The computed relative activation energies for the Diels−Alder reaction of cyclopentadiene with all of the cyanoethylenes were also reported by Hehre.[8] The performance of methods was analyzed by comparison to activation energies calculated with a standard reference, MP2/6-311+G(d,p). HF with 3-21G and 6-31G(d) basis sets and MP2 with the 6-31G(d) basis give excellent relative activation energies in these systems. The BP, BLYP and EDF1 functionals were less satisfactory and gave the wrong trend for tricyanoethylene and TCNE. Hehre's report was an important stimulus for this work. AM1 and PM3 predict that increasing the number of cyano groups increases the activation barrier, which is an effect opposite to experimental results.[8]

While this study was in progress, Domingo et al. reported a study of the Diels−Alder reactions of cyclopentadiene with polycyanoethylenes.[9] B3LYP/6-31G(d) failed to predict correctly the substituent effects of tricyanoethylene and tetracyanoethylene. No explanation was offered for this curious failure, which was the same as that observed earlier by Hehre.[8]

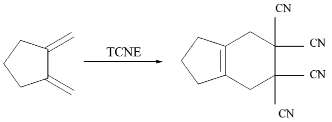
Charge-Transfer Complexes. For the most electron-deficient dienophile, TCNE, a charge-transfer complex (CT) has been found experimentally.[13−16] This could be an intermediate along the reaction path (eq 1) or a complex formed in an equilibrium side reaction and not directly involved in the reaction (eq 2).

$$A + B \rightleftharpoons AB_{CT} \rightleftharpoons P \tag{1}$$

$$AB_{CT} \rightleftharpoons A + B \rightleftharpoons P \tag{2}$$

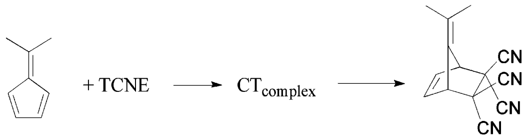
There have been many studies on CT complexes of anthracene and TCNE.[11,17−19] Andrews and Keefer pointed out that the kinetics of the disappearance of anthracene and TCNE at a single temperature could not distinguish between these mechanisms.[20] Kiselev and Miller proposed that solvent effects on cycloaddition reactions and the negative activation enthalpy observed at some temperatures constitute evidence for the CT complex as an intermediate.[12]

Sustmann et al. determined activation parameters for the cycloaddition of 1,2-dimethylenecyclopentene to tetracyanoethylene at 0 and 20 °C.[21]



The kinetic analysis of the disappearance of reactants and the CT complex could be interpreted either according to the scheme in which the CT complex is an intermediate on the reaction path or existed as a nonreactive complex in equilibrium with reactants. In connection with Andrews and Keefer's work,[20] Sustmann and co-workers found a more negative activation entropy for the decay of the CT complex than for the disappearance of the reactants. They suggest that this behavior is unexpected if the CT complex is an intermediate in the reaction, and concluded that the CT complex is not a preorientation complex in the cycloaddition.

While our investigations were in progress, Howard and co-workers published a theoretical study on the formation of CT complexes between 6,6-dimethylfulvene with tetracyanoethylene.[22]



B3LYP/6-31G(d) results showed that a CT complex is stabilized by 7.8 kcal/mol and the activation barrier is 11.4 kcal/mol.

Computational Methods. Calculations were performed with the Gaussian 98 and Gaussian 03 suites of computational programs.[23] All reactants, transition states, and products were optimized with HF, hybrid DFT methods with the gradient-corrected functionals B3LYP,[24,25] MPW1K[26] and the nonhybrid DFT method, BPW91.[27] The 6-31G(d) basis set was used in calculations involving the HF, B3LYP, and BPW91 methods. The 6-31+G(d,p) basis set was used for MPW1K and B3LYP calculations.

The effect of solvent was explored with the Cosmo Polarizable Continuum Model (CPCM)[28] for benzene solvent with the B3LYP and MPW1K methods. All of the minima and transition states were characterized by calculations of vibrational frequencies.

B3LYP is the most widely used density functional and is a combination of the Dirac−Slater exchange term,[29] Becke's 1988 nonlocal exchange functional (B88),[27a] Vosko, Wilk, and Nusair's local correlation functional III (VWN3),[30] Lee, Yang, and Parr's (LYP) nonlocal correlation functional,[27b] and 20% of exact (Hartree−Fock) exchange.

MPW1K is a hybrid HF-density functional method, developed by Truhlar et al. termed the modified Perdew−Wang 1-parameter model for kinetics.[26] This method includes 42.8% Hartree−Fock exchange.

BPW91 involves the Becke nonhybrid exchange functional, and the Perdew−Wang-1991 (PW91) gradient-corrected correlation functional replaces the LYP functional.[27a,31]

Energies and distances are given in units of kcal/mol and Ångstroms, respectively. All of the optimizations have been computed at standard temperature and pressure. Reported frequencies were unscaled.

TABLE 4: Activation Barriers for Endo Diels−Alder Reactions of Cyclopentadiene with Cyanoethylenes[a]

	$\Delta H^{\ddagger}$				
	HF[b]	B3LYP[b,c]	BPW91[b]	MPW1K[c]	exptl
none	42.0	22.3, (23.5) [18.7]	19.3	20.7 [19.8]	22.5[e]
CN	37.8	18.9, (19.5) [15.4]	13.8	16.3 [15.2]	15.5[d]
trans-1,2-$(CN)_2$	34.4	16.5, (17.9) [14.0]	14.4	12.9 [12.4]	12.8[d]
cis-1,2-$(CN)_2$	34.5	17.0, (18.3) [14.3]	13.2	13.4 [12.4]	12.8[d]
1,1-$(CN)_2$	30.0	11.2, (12.7) [7.4]	8.6	8.9 [7.1]	9.0[d]
1,1,2-$(CN)_3$	28.0	11.9, (13.3) [8.6]	10.1	7.7 [6.1]	7.6[d]
1,1,2,2-$(CN)_4$	26.1	12.1, (13.5) [8.5]	11.0	5.6 [4.1]	5.0[d]

[a] Activation energies corrected with benzene solvation energies are given in brackets below gas-phase numbers, B3LYP energies determined with the 6-31+G(d,p) basis set are given in parentheses. [b] 6-31G(d). [c] 6-31+G(d,p). [d] Estimated from experimental $\Delta\Delta H^{\ddagger}$ value, see Table 1. [e] Gas phase, 521−570 K, Walsh, R.; Wells, J. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 52.

Results and Discussion

Activation Enthalpies: Cyclopentadiene. Activation enthalpies calculated with HF, hybrid-DFT methods (B3LYP, BPW91, MPW1K) for formation of the endo transition states of cyclopentadiene with cyanoethylenes are given in Table 4 along with the best experimental values. Solvent-corrected calculations with the MPW1K and B3LYP methods are also given.

Figure 1 is a plot of the computational activation enthalpies versus experimental values to show how well substituent effects are reflected by computational methods. Figure 2 shows a graph of computed and experimental barriers for the Diels−Alder reaction of cyclopentadiene with ethylene and the cyanoethylenes.

Comparison of computed and experimental activation enthalpies of the Diels−Alder reaction of cyclopentadiene with cyanoethylenes (Figure 1) reveals that HF and MPW1K provide the best linear correlations ($R^2 = 0.95$ in both cases). MPW1K has an intercept close to 0 kcal/mol (1.7 kcal/mol) and a slope of 0.88. HF overestimates activation barriers by a nearly constant 21.6 kcal/mol because of neglect of electron correlation, but the slope of this correlation is very near to 1, and HF reproduces $\Delta\Delta H^{\ddagger}$ very well. The B3LYP and BPW91 density functionals have very low slopes of 0.67 and 0.54, respectively.

When the 6-31+G(d,p) basis set is used with the B3LYP method, the slope is almost identical to that seen with the smaller basis set, 6-31G(d), and the correlation is also similar at $R^2 = 0.87$. With 6-31+G(d,p), the intercept is 9.3 kcal/mol, versus 7.8 kcal/mol obtained with the 6-31G(d) basis set, indicating a systematic overestimation of transition state energies by 1.5 kcal/mol over predictions obtained with the smaller basis set.

Figure 2 is an alternative way to compare experiment to theory. It shows more clearly that, B3LYP and BPW91, which have poor slopes, also fail to predict the correct trends for tricyano and tetracyanoethylene with respect to dicyanoethylenes. MPW1K with solvation is, within experimental error, perfect, and HF with a 21.6 kcal/mol correction for correlation error is also excellent. In accordance with experimental results,

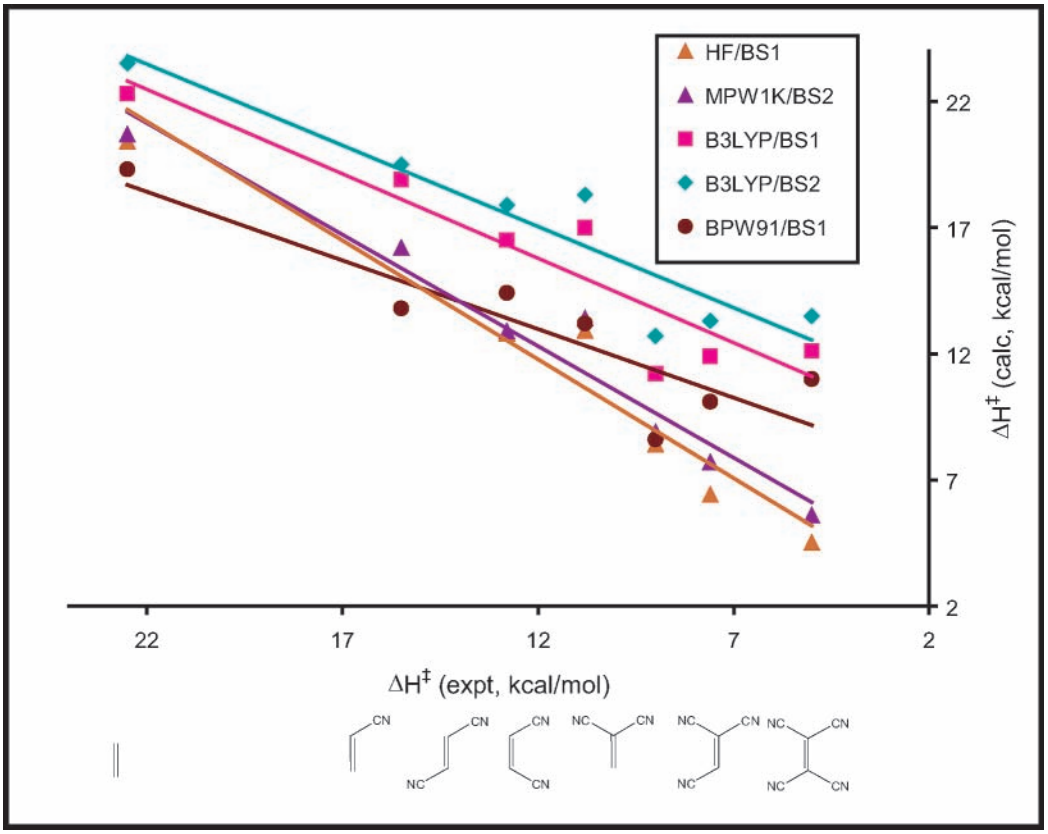


Figure 1. Plot of computed activation enthalpies vs experimental activation enthalpies for Diels−Alder reaction of cyclopentadiene with cyanoethylenes. The linear regressions obtained are shown. HF/BS1: $y = 0.94x + 0.57$, $R^2 = 0.95$. MPW1K/BS2: $y = 0.88x + 1.7$, $R^2 = 0.95$. B3LYP/BS1: $y = 0.67x + 7.8$, $R^2 = 0.87$. B3LYP/BS2: $y = 0.64x + 9.3$, $R^2 = 0.87$. BPW91/BS1: $y = 0.54x + 6.4$, $R^2 = 0.80$. [BS1:6-31G(d), BS2 = 6-31+G(d,p).]

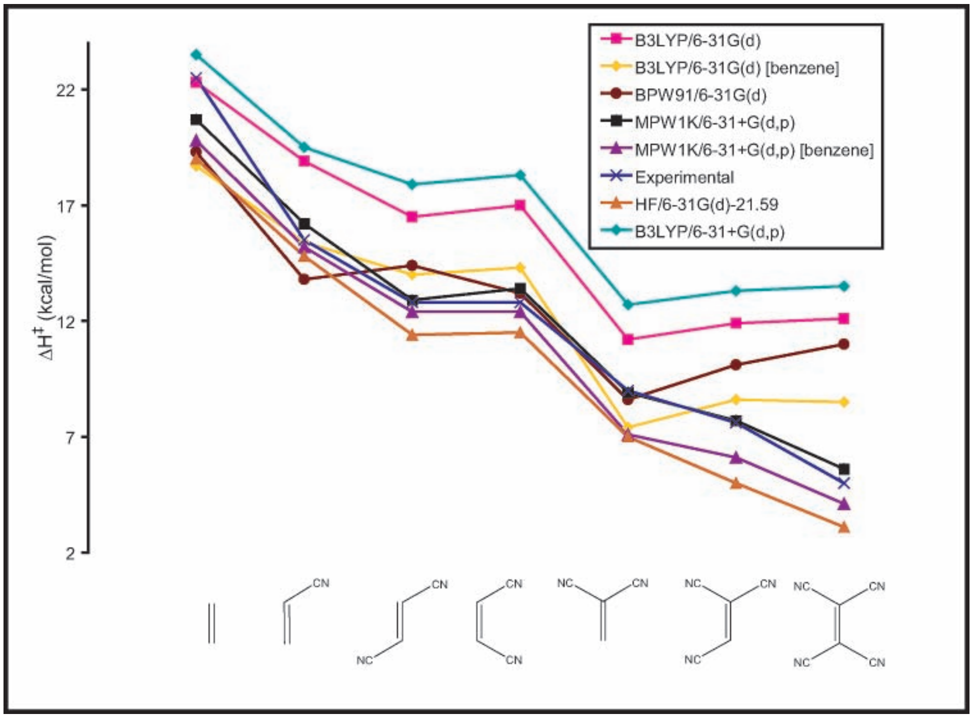


Figure 2. Comparison of calculated enthalpy of activation at different levels with experimental activation barriers.

all methods predict that the activation barrier for the reaction of cyclopentadiene with 1,1-dicyanoethylene is much lower than that of the other dicyanoethylenes.

BPW91 exhibits very similar behavior to B3LYP, but in addition to a failure to predict the substituent effects for tri- and tetracyanoethylene, it also fails to account for the rate increase on going from cyanoethylene to *trans*-1,2-dicyanothylene.

As the number of cyano groups increases, the charge separation in the transition state increases. Figures 1 and 2

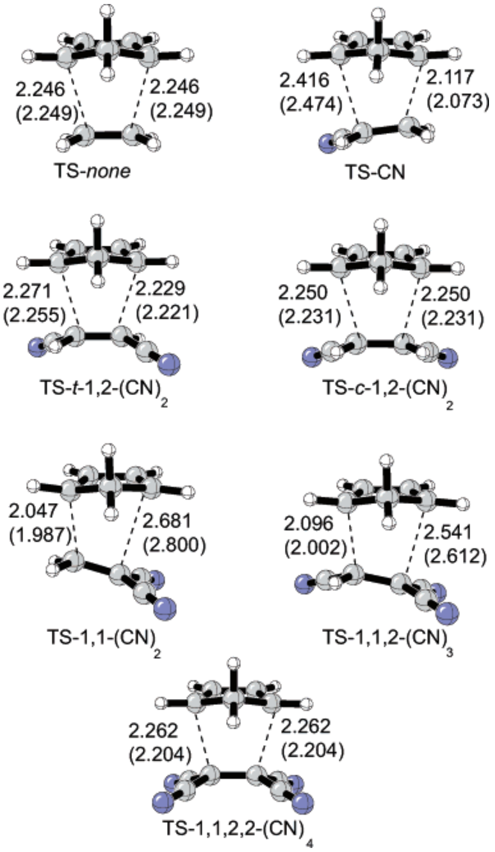


Figure 3. MP1WK optimized geometries of transition structures leading to endo-product formation for the Diels−Alder reactions of cyclopentadiene with cyanoethylenes (values in parentheses are B3LYP/6-31G(d) bond distances).

suggest that methods with large amounts of exact exchange, such as HF and MPW1K, predict activation energies correctly, even for large charge separation, whereas those with less exact exchange underestimate the substituent effect. Truhlar specifically increased the amount of exact exchange to improve barriers with MPW1K. This may be a general problem with systems involving significant charge separation, and we are testing this with other systems.

Solvent effects were also considered because these kinetic studies were done in dioxane. Gaussian 98 CPCM calculations were performed for solvation energies with benzene, which has similar characteristics to dioxane. Activation barriers computed with these solvation corrections are better correlated with experimental barriers than gas-phase numbers.

Transition State Geometries. Figures 3 and 4 show MPW1K endo- and exo-transition state geometries, respectively, for the reactions of cyclopentadiene with ethylene and cyanoethylenes. The remaining geometrical information is given in the Supporting Information.

Table 5 gives forming bond lengths *a* and *b* obtained at various levels of theory. With the exception of tetracyanoethylene, HF theory gives bond lengths that are too short for the transition states of cyclopentadiene with ethylene and cyanoethylenes. HF tends to predict forming bond lengths incorrectly because of a lack of electron correlation. For the symmetric dienophiles, ethylene and 1,2-dicyanoethylene, BPW91 gives the longest bond lengths.

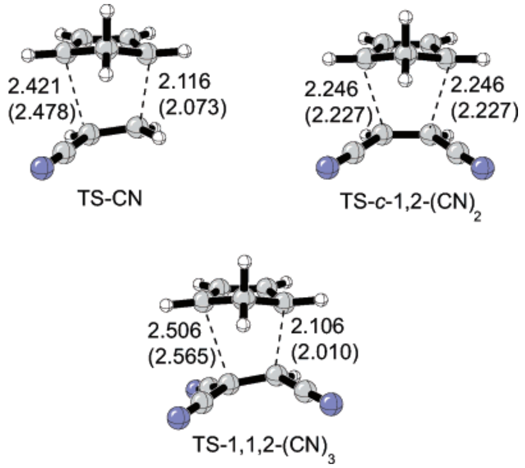
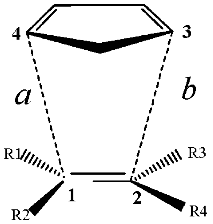


Figure 4. MP1WK optimized geometries of transition structures leading to exo-product formation for the Diels−Alder reactions of cyclopentadiene with cyanoethylenes (values in parentheses are B3LYP/6-31G(d) bond distances).

TABLE 5: Bond Lengths, *a* and *b*, for Transition Structures of Diels−Alder Reactions between Ethylene and Cyanoethylenes with Cyclopentadiene



	stereo-chemistry	bond	HF^a	B3LYP^a	BPW91^a	MPW1K^b
none		*a*	2.193	2.249	2.304	2.246
		b	2.193	2.249	2.304	2.246
1-CN	endo	*a*	2.316	2.474	2.586	2.416
		b	2.091	2.073	2.108	2.117
	exo	*a*	2.325	2.478	2.584	2.421
		b	2.090	2.073	2.109	2.116
1,1-(CN)$_2$		*a*	2.622	2.800	2.920	2.681
		b	1.951	1.987	2.077	2.047
cis-1,2-CN)$_2$	endo	*a*	2.204	2.231	2.272	2.250
		b	2.204	2.231	2.272	2.250
	exo	*a*	2.209	2.227	2.263	2.246
		b	2.209	2.227	2.263	2.246
trans-1,2-(CN)$_2$		*a*	2.227	2.255	2.293	2.266
		b	2.202	2.221	2.264	2.248
1,1,2-(CN)$_3$	endo	*a*	2.012	2.002	2.040	2.096
		b	2.554	2.612	2.689	2.541
	exo	*a*	2.495	2.565	2.645	2.506
		b	2.038	2.010	2.031	2.101
1,1,2,2-(CN)$_4$		*a*	2.242	2.204	2.220	2.262
		b	2.242	2.204	2.220	2.262

^{a} 6-31G(d). ^{b} 6-31+G(d,p).

For the asymmetrically substituted ethylenes, 1-cyano-, 1,1-dicyano, and 1,1,2-tricyanoethylene, highly asynchronous transition structures are found. Differences between *a* and *b* in the transition structure of 1,1-dicyanoethylene with cyclopentadiene are 0.84 Å (BPW91), 0.81 Å (B3LYP), 0.67 Å (HF), and 0.63 Å (MPW1K). Note that the methods that give better activation barriers also give more synchronous transition structures.

As indicated in Table 5, for acrylonitrile, the order of differences in bonds *a* and *b* is HF < MPW1K < B3LYP < BPW91, but for 1,1-dicyano- and 1,1,2-tricyanoethylene, it is MPW1K < HF < B3LYP < BPW91. The increase in the degree of asynchronicity of the transition states can also be seen with the less accurate methods.

Charge Separation at the Transition State. The amount of charge transferred from the electron-rich diene to the electron-deficient alkene dienophiles in the transition state was evaluated

TABLE 6: Sum of CHelpG Charges, Q^a, on the Atoms of Dienophiles at the Transition State of the Diels−Alder Reaction between Cyanoethylenes and Cyclopentadiene[b]

	stereochemistry	HF[c]	B3LYP[c]	BPW91[c]	MPW1K[d]
1-CN	endo	−0.16	−0.15	−0.15	−0.16
		(−0.16)	(−0.15)	(−0.15)	(−0.21)
	exo	−0.15	−0.15	−0.14	−0.15
		(−0.16)	(−0.15)	(−0.15)	(−0.21)
1,1-(CN)$_2$		−0.24	−0.23	−0.22	−0.24
		(−0.33)	(−0.28)	(−0.25)	(−0.34)
cis-1,2-(CN)$_2$	endo	−0.22	−0.23	−0.22	−0.23
		(−0.25)	(−0.24)	(−0.23)	(−0.35)
	exo	−0.22	−0.22	−0.22	−0.23
		(−0.25)	(−0.24)	(−0.23)	(−0.35)
trans-1,2-(CN)$_2$		−0.23	−0.23	−0.23	−0.23
		(−0.26)	(−0.25)	(−0.24)	(−0.35)
1,1,2-(CN)$_3$	endo	−0.29	−0.28	−0.27	−0.28
		(−0.40)	(−0.36)	(−0.34)	(−0.48)
	exo	−0.29	−0.28	−0.27	−0.29
		(−0.39)	(−0.35)	(−0.34)	(−0.47)
1,1,2,2-(CN)$_4$		−0.34	−0.35	−0.34	−0.35
		(−0.42)	(−0.42)	(−0.41)	(−0.66)

[a] In units of *e*. [b] Mulliken charges in parentheses. [c] 6-31G(d). [d] 6-31+G(d,p).

with Mulliken Population Analysis and CHelpG charges derived from electrostatic potentials.

Table 6 shows that the increase in charge separation with the addition of cyano groups is more dramatic when Mulliken population analysis is used to assess transition state charges. Mulliken charges of MPW1K transition states are greater than corresponding ones at the HF, B3LYP, and BPW91 levels. However, the CHelpG method presents a more consistent picture of the charges with all of the different methods.

As expected, with the addition of electron-withdrawing groups on the dienophile the charge separation increases in a systematic manner, reflecting the increasing zwitterionic character of the transition states. Charge separation of a relatively modest 0.15 *e* for the reaction of cyclopentadiene with cyanoethylene increases to a larger 0.35 *e* (depending on the calculation used) for the reaction of cyclopentadiene with TCNE. The reactivities of the cyanoethylenes correlate with increasing charge separation. Interestingly, the DFT method that predicts reactivities correctly has exaggerated Mulliken charge separations.

Endo/exo Selectivity. Endo selectivity in the cycloaddition of cyclopentadiene with acrylonitrile has been observed experimentally by Sauer et al.[32] The ratio changes from 1.1 in dioxane (dielectric constant = 2.2) to 2.2 in the more polar acetonitrile (dielectric constant = 38.3). As shown in Table 7, all DFT methods, B3LYP, BPW91, and MPW1K, predict the activation enthalpy for exo cycloaddition to be 0.3−0.9 kcal/mol lower than endo in the gas phase. The HF method predicts that the endo stereochemistry is favored by 0.1 kcal/mol. Activation energies provided by the B3LYP and MPW1K methods in benzene (dielectric constant = 2.3) also predict that the exo stereochemistry is favored by ∼0.3 kcal/mol.

HF favors endo transition states in reactions of cyclopentadiene with *cis*-1,2-dicyanoethylene and 1,1,2-tricyanoethylene in the gas phase. However, B3LYP predicts that in both cases exo transition states are favored by 0.2 kcal/mol. When benzene is the solvent, exo selectivity is still favored for the reaction of *cis*-1,2-dicyanoethylene with cyclopentadiene, however, endo selectivity is predicted for the corresponding reaction with 1,1,2-tricyanoethylene.

MPW1K predicts that the exo transition state of the reaction of cyclopentadiene with *cis*-1,2-dicyanoethylene is favored by 1.9 kcal/mol in the gas phase. However, this difference decreases to 0.1 kcal/mol with a dioxane solvent correction. Although MPW1K predicts that there is no difference in selectivity for the reaction of 1,1,2-tricyanoethylene with cyclopentadiene in the gas phase, correction with benzene solvation energies causes a shift toward formation of the endo adduct.

TABLE 7: Comparison of Computed Activation Enthalpies for Endo- and Exo Diels−Alder Reactions of Cyclopentadiene with Cyanoethylenes in Gas Phase and Dioxane Solvent at 298 K[a]

		$\Delta H^\ddagger$			
	stereochemistry	HF[d]	B3LYP[d]	BPW91[d]	MPW1K[e]
CN	endo[b]	37.8	19.0	13.8	16.3
	exo	37.9	18.1	13.3	16.0
	endo[c]		15.4		15.2
	exo		15.0		15.0
cis-1,2-(CN)$_2$	endo[b]	34.5	17.0	13.2	13.4
	exo	34.8	16.7	12.5	11.3
	endo[c]		14.3		12.4
	exo		14.1		12.5
1,1,2-(CN)$_3$	endo[b]	28.1	11.9	10.1	7.7
	exo	28.6	12.1	8.4	7.7
	endo[c]		8.6		6.1
	exo		8.8		6.3

[a] Energies in kcal/mol. [b] Gas phase. [c] Benzene. [d] 6-31G(d) [e] 6-31+G(d,p).

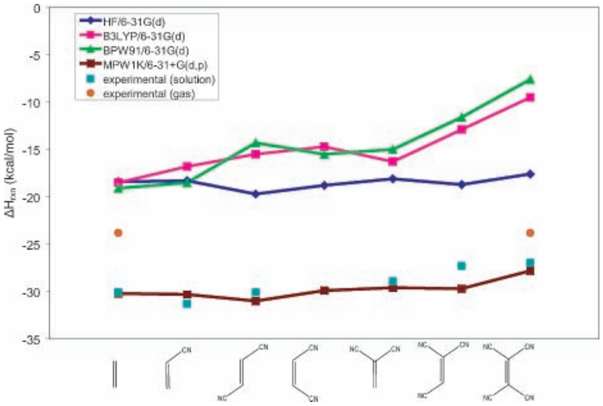


Figure 5. Comparison of calculated heats of reaction of ethylene and cyanoethylenes with cyclopentadiene at different levels at 298 K with experimental values.

Endo selectivity is not predicted in the reaction of cyclopentadiene with acrylonitrile in the gas phase by any method but HF, which favors only slight endo selectivity of 0.1 kcal/mol, which is within computational error. Solvent correction of the B3LYP and MPW1K methods reduces the difference between endo and exo activation barriers but does not alter the preference for exo selectivity.

Enthalpies of Reaction. In Figure 5 and Table 8, the heats of reaction computed by various methods are compared with the few known experimental values. There are two experimentally determined gas phase heats of reaction in the cyano series for the reactions of cyclopentadiene with ethylene and tetracyanoethylene.[33] Both reactions are exothermic by approximately 23 kcal/mol. The experimentally determined reaction enthalpies in solution are known for the reactions of cyclopentadiene with all of the alkenes studied here except for *cis*-1,2-dicyanoethylene.[34] These ΔH_{rxn} values range from −27 to −31.3 kcal/mol.

The HF and MPW1K methods seem to predict the trends in the solvated and gas phase ΔH_{rxn} values correctly. However, HF underestimates the exothermicity of the gas-phase values by about 5 kcal/mol, whereas MPW1K overestimates ΔH_{rxn} values by the same amount. MPW1K predicts reaction enthalpies

TABLE 8: Computed and Experimental Heats of Reaction (ΔH_{rxn}) in the Gas Phase and Solvent for Endo and Exo Products of the Diels−Alder Reactions of Cyclopentadiene with Ethylene and Cyanoethylenes[a]

	stereo-chemistry	ΔH_{rxn}				
		HF[b]	B3LYP[b]	BPW91[b]	MPW1K[c]	exptl
none		−18.4	−18.5	−19.1	−30.2	−23.8[d]
			(−26.2)		(−31.9)	
CN	endo	−18.3	−16.8	−18.5	−30.3	(−31.3)[e]
	exo	(−18.4)	(−16.9)	(−18.7)	(−30.4)	
			−23.2		−31.7	
			(−23.2)		(−31.7)	
trans-1,2-$(CN)_2$		−19.7	−15.5	−14.3	−31.0	(−30.1)[e]
			(−21.0)		(−31.4)	
cis-1,2-$(CN)_2$	endo	−18.8	−14.7	−15.5	−29.9	
	exo	(−18.5)	(−14.6)	(−15.4)	(−31.7)	
			−20.7		−31.4	
			(−20.3)		(−31.3)	
1,1-$(CN)_2$		−18.1	−16.3	−15.0	−29.6	(−28.9)[e]
			(−21.0)		(−31.0)	
1,1,2-$(CN)_3$	endo	−18.7	−12.9	−11.6	−29.7	(−27.3)[e]
	exo	(−18.3)	(−12.7)	(−13.1)	(−29.4)	
			−18.5		−30.0	
			(−18.1)		(−30.4)	
1,1,2,2-$(CN)_4$		−17.6	−9.5	−7.6	−27.8	−23.8
			(−15.1)		(−29.6)	(−27.0)[e]

[a] Energies are in kcal/mol. Heats of reaction in solution are given in parentheses below gas-phase numbers (calculated energies are corrected with benzene solvation energies). [b] 6-31G(d). [c] 6-31+G(d,p). [d] Estimated, see ref 33. [e] 298 K, see ref 34.

TABLE 9: Computed and Experimental Activation Enthalpies for Diels−Alder Reactions of 9,10-dimethylanthracene with Cyanoethylene and TCNE

	$\Delta H^{\ddagger}$			
	HF[a]	B3LYP[a]	MPW1K[b]	exptl
CN	38.4		14.8	15.0[c]
1,1,2,2-$(CN)_4$	24.6	12.7	−1.2	1.2[d]
				−1.5[e]
				4.4[f]
				2.9[f]
				1.7[f]
				−1.9[f]

[a] 6-31G(d). [b] 6-31+G(d,p). [c] In dioxane, 293 K, see ref 1. [d] Estimated from $\Delta\Delta H^{\ddagger}$ value. [e] CCl_4, 298 K, ref 19. [f] Top to bottom: *o*-xylene, toluene, benzene, (all at temperatures ranging from 286 to 313 K) and dichloromethane (285 to 298 K); ref 12.

that are, within experimental error, in almost perfect agreement with the experimentally determined solution phase reaction enthalpies.

HF, B3LYP, and BPW91 all underestimate the exothermicity of the Diels−Alder reaction with acrylonitrile, and larger errors occurring with the addition of more cyano groups. The results with tricyano and tetracyano substituents are especially poor, consistent with the errors in $\Delta\Delta H^{\ddagger}$ values noted earlier.

Activation Enthalpies: 9,10-Dimethylanthracene. Activation enthalpies for the reactions of cyanoethylene and tetracyanoethylene with 9,10-dimethylanthracene computed by HF and MPW1K methods are presented in Table 9. B3LYP was also tested for the reaction of dimethylanthracene and TCNE. HF overestimates activation barriers by about 22 kcal/mol in both cases, consistent with the electron correlation error noted earlier. Interestingly, B3LYP also overestimates the activation barrier for the reaction of dimethylanthracene and TCNE, whereas MPW1K predicts that the activation enthalpy is −1.2 kcal/mol, which is close to the experimental result.

Figure 6 shows that the reaction of 9,10-dimethylanthracene with cyanoethylene has an asymmetric transition structure, whereas that with TCNE is symmetric. The forming bond lengths are longer than those seen in the reactions of cyclopentadiene with cyano- and tetracyanoethylene.

Figure 6. MPW1K optimized geometries of the transition structures of the Diels−Alder reactions of 9,10-dimethylanthracene with cyanoethylene and tetracyanoethylene (values in brackets are for HF/6-31G*).

Charge-Transfer Complexes with TCNE. Scheiner et al. have located the CT complex of anthracene-tetracyanoethylene (AN-TCNE) previously with various density functionals.[35] The CT complex was constructed by placing one component parallel to the other, consistent with crystal structures, for related complexes, and then optimizing. B3LYP predicted that the intermolecular distance between the two is 3.44 Å and the binding energy is 5.5 kcal/mol, a value that overestimates the stability of the experimental binding energy of 2.1 kcal/mol.

Wise and Wheeler have reported that B3LYP predicts the binding energy of AN-TCNE to be −5.2 kcal/mol with the 6-31G(d) basis set and −3.8 kcal/mol with the 6-31+G(d,p) basis set.[36] These values are close to the experimentally determined value of −3.5 kcal/mol. In the case of 9,10-dimethylanthracene, the experimental binding energy is −5.6 kcal/mol, which is larger than that of anthracene by 2.4 kcal/mol.[19]

Charge transfer (CT) complexes of cyclopentadiene (CP), anthracene (AN), and 9,10-dimethylanthracene (DMAN) with tetracyanoethylene (TCNE) have been explored here by HF, B3LYP, and MPW1K methods.

MPW1K optimized geometries of CT complexes are given in Figure 7. The CT complex of CP-TCNE has been located for the first time.

The binding enthalpies have been calculated for the CT complexes of CP-TCNE, AN-TCNE, and DMAN-TCNE and are provided in Table 10 along with R_{A-D}, the intermolecular distance between atoms that interact in both species, and the sum of Mulliken charges on the acceptor molecule, Q_A.

The R_{A-D} values for the CT complex of CP-TCNE presented in Table 10 range from 3.23 (MPW1K) to 3.75 Å (HF). These

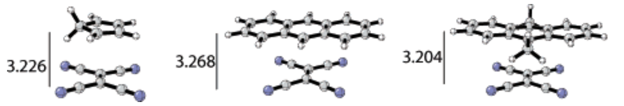


Figure 7. MP1WK/6-31+G(d,p) optimized geometries and intermolecular distances (left of structure) for CT complexes of TCNE with CP, AN, and DMAN.

TABLE 10: Binding Enthalpies, Intermolecular Distances, and CHelpG Charges on the acceptor molecule, Q_A,[a] for CT Complexes of TCNE with Cyclopentadiene (CP), Anthracene (AN), and 9,10-Dimethylanthracene (DMAN)[b]

	CP	AN	DMAN
H_{bind} (kcal/mol)			
HF[f]	−2.1	−2.2	−2.5
B3LYP[f]	−3.3	−4.5	−7.0
MPW1K[g]	−0.7	−1.8	−10.7
exptl	-	−3.2[c]	−5.6[c]
$R_{\mathrm{A-D}}$ (Å)[d]			
HF	3.750	3.809	3.717
B3LYP	3.361	3.409[e]	3.276
MPW1K	3.226	3.268	3.204
Q_A (e)			
HF	−0.03	−0.06	−0.07
	(−0.02)	(−0.02)	(−0.03)
B3LYP	−0.06	−0.13	−0.19
	(−0.11)	(−0.20)	(−0.26)
MPW1K	−0.08	−0.15	−0.20
	(−0.25)	(−0.21)	(−0.31)

[a] Mulliken charges in parentheses. [b] Energies as compared to reactants. [c] CCl_4, 298 K, ref 19. [d] $R_{\mathrm{A-D}}$ is the distance between terminal atoms of reactant molecules. [e] Reference 39. [f] 6-31G(d). [g] 6-31+G(d,p).

values are ~1 (MPW1K) to ~1.5 Å (HF) greater than the distances between the forming bonds of the transition structure (Table 5 and Figure 6) but are consistent with the 3.4-Å interlayer distances commonly cited for graphite and other $\pi-\pi$ complexes.

HF predicts that nearly equal amounts of Mulliken charge is transferred by all three dienes to TCNE; these Mulliken charges are less than the CHelpG charges predicted by HF. The Mulliken charges of the complexes computed by the B3LYP and MPW1K methods are greater than those predicted by the CHelpG electrostatic potentials. B3LYP predicts that the amount of CHelpG charge transferred increases from −0.06 e, for CP-TCNE, to −0.19 e for DMAN-TCNE. The magnitude of the MPW1K CHelpG charges is similar to that found for B3LYP, and a similar increase in the amount of charge transfer is also seen on going along the series of dienes. Notably, MPW1K predicts that the amount of Mulliken charge transferred by cyclopentadiene is greater than that seen for anthracene, which runs counter to expectations. However, DMAN is predicted by MPW1K to transfer greater amounts of Mulliken charge than CP or AN in the CT complex. As was seen before when evaluating transition-states, the CHelpG method seems to make more consistent predictions of the charges transferred from diene to dienophile than Mulliken population analysis.

The binding enthalpy for AN-TCNE is predicted to be 1.2 kcal/mol higher than for the CP-TCNE complex by the MPW1K method, presumably because of weak $\pi-\pi$ interactions of the nonreacting aromatic rings in anthracene with the cyano groups in TCNE. The DMAN-TCNE complex is computed by B3LYP to be ~1.5 kcal/mol more stable than AN-TCNE. However, MPW1K predicts that DMAN-TCNE is more stable than AN-TCNE by 8.9 kcal/mol. Shorter $R_{\mathrm{A-D}}$ distances for DMAN-TCNE than AN-TCNE suggests that electron donation from the methyl groups into the diene π system contributes to increasing charge separation and stability of the CT complex.

Conclusions

The performance of HF and the hybrid-DFT methods, B3LYP, BPW91, and MPW1K, has been evaluated for predictions of substituent effects on kinetics and thermodynamics of Diels−Alder reactions between cyclopentadiene and 9,10-dimethylanthracene and the series of cyanoethylenes.

MPW1K and HF methods reproduce substituent effects on activation energies very well, although HF overestimates activation barriers by a consistent ~22 kcal/mol. MPW1K gives the best qualitative and quantitative results of all of the methods investigated here. B3LYP and BPW91 predict that 1,1-dicyanoethylene is the best dienophile in reactions with cyclopentadiene followed by tricyanoethylene and tetracyanoethylene, which is not in agreement with experimental results. Both methods overestimate activation barriers and underestimate the activation energy lowering by cyano groups.

B3LYP overestimates the activation enthalpy of the reaction between 9,10-dimethylanthracene and TCNE by ~13 kcal/mol. Taken in their entirety, these results suggest that as the diene or dienophile becomes increasingly electron-deficient B3LYP is less able to describe these substituent effects on either rates or reaction energies. BPW91 has a similar problem, and only methods with more exact exchange seem capable of treating the systems with substantial charge separation in the transition state properly. We are exploring if this is a general problem and what the origin might be.

Here we note that Truhlar and co-workers have observed that MPW1K predicts barrier heights remarkably well compared to other methods, a result in agreement with this study, but gives poor results for thermochemical predictions.[37] We have found that MPW1K makes better predictions for the substituent effect on the heats of reaction than other methods, especially in the case of tricyano- and tetracyanoethylene.

The CT complexes of tetracyanoethylene with cyclopentadiene, anthracene, and 9,10-dimethylanthracene have been investigated by HF, B3LYP, and MPW1K. B3LYP provides satisfactory values for complex stability, whereas HF shows that there is very little variation among the stability of complexes.

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Supporting Information Available: MPW1K optimized Cartesian coordinates and electronic energies (hartrees) for reactants and transition structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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