

Improved Reaction and Activation Energies of [4+2] Cycloadditions, [3,3] Sigmatropic Rearrangements and Electrocyclizations with the Spin-Component-Scaled MP2 Method

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Abstract: A new quantum mechanical scheme to calculate electronic correlation energies, spin-component-scaled MP2, was tested as a tool to predict reaction energies and barriers in computational organic chemistry. Three common pericyclic reactions with known unsatisfactory MP2 descriptions were reinvestigated with the modified MP2 approach, in which the parallel and anti-parallel spin components of the correlation energy are scaled separately.

The SCS-MP2 calculated reaction and activation energies of nine Diels–Alder reactions, four [3,3] sigmatropic rearrangements, and ten electrocyclization reactions are compared to

those of the MP2, B3LYP, QCISD(T), and G3 methods. For each, the SCS-MP2 results are in excellent agreement with the experimental data and compare far more favorably to G3 than both MP2 and B3LYP. Careful evaluation of the effect of the size of the atomic orbital (AO) basis set shows that the larger expansions improve the agreement with experiment for the SCS-MP2 method, while they get worse for both MP2 and B3LYP.

Keywords: ab initio calculations • Cope rearrangement • Diels–Alder reaction • electrocyclization reaction • heterocycles • pericyclic reaction

Introduction

Accurately predicting reaction energies and activation barriers for pericyclic reactions remains a challenge for ab initio theoretical methods.^[1] These reactions, which are of immense importance to organic chemists, are usually composed of too large a number of atoms to be amenable to the best composite methods, like G3,^[2] or those that treat multi-configurational and dynamical electron correlation accurately (e.g., multireference CI). Neither can these reactions be treated by simple schemes that rely on the cancellation of errors, like isodesmic^[1] and homodesmotic^[3] reactions, to

minimize the effect of neglect of electron correlation, because of the changing type and/or number of bonds. By far the most popular method that includes electron correlation has been second-order Møller–Plesset perturbation theory (MP2),^[4] before the recent advancement of density functional theory (DFT).^[5] However, both methods have their shortcomings in treating pericyclic reactions. For example, DFT often underestimates barrier heights^[6,7] and overestimates π -conjugative effects,^[7,8] and MP2 uses an unbalanced treatment of electron correlation (vide infra).

Recently, one of us showed that a simple and logical correction to the MP2 scheme leads to significant improvements in cases in which MP2 underperforms.^[9,10] The correction is based on a different scaling of the spin-parallel (E_i) and spin-antiparallel (E_s) electron pair contributions to the correlation energy, $E_c = p_s E_s + p_i E_i$, with p_s and p_i scaling factors of 6/5 and 1/3, respectively. This spin-component-scaled MP2 approach (SCS-MP2) differs from MP2, in which both components contribute equally. It was shown that the simple correction in scaling gives performances in reaction energies comparable to the QCISD(T) method.^[11] This success is easily traced to the manner in which the dynamic (spin-antiparallel) and static (spin-parallel) correlation effects are introduced. In the Hartree–Fock method the spin-parallel electron pairs are correlated (Fermi holes), while the spin-antiparallel pairs remain uncorrelated. Low (second) order

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perturbation theory cannot fully correct for this unbalanced description. Hence, the non-HF-correlated pair contribution must be scaled-up, while the HF-correlated contribution must be scaled-down.

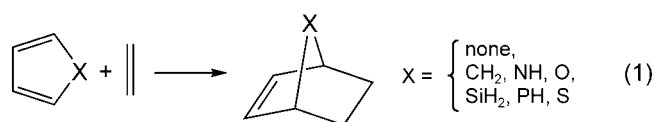
Inspired by the remarkable improvement of SCS-MP2 over MP2 for the prediction of reaction energies for simple organic systems,^[9] we wondered about its performance for the computationally challenging pericyclic processes, which are still scrutinized extensively to find the most appropriate theoretical method.^[12] In this study we will show that SCS-MP2 calculated reaction energies and activation barriers for Diels–Alder reactions, [3,3] sigmatropic rearrangements, and electrocyclization reactions^[13] compare very favorably with experimental data and those obtained with the G3 method, and that they are far superior to those obtained with both B3LYP and conventional MP2.

Results and Discussion

For each of the following [4+2] cycloaddition, [3,3] sigmatropic shift, and electrocyclic reactions we discuss the performance of SCS-MP2 against the MP2(full), B3LYP, and G3 methods and available experimental data. QCISD(T) energies are provided for completeness, because the reported scaling parameters of SCS-MP2 are calibrated against this method.^[9] Two basis sets were used, a small one, labeled S, for 6-31G*, and a large one, labeled L, for 6-311++G(3df,3pd) to evaluate their influence. The 6-311++G(3df,3pd) basis is of similar size as the G3Large basis set used in the G3 procedure to extrapolate the correlation energy to the basis set limit. Scaled HF/6-31G* zero point energy (ZPE) corrections ($F=0.8929$)^[14] were applied to all HF, MP2, SCS-MP2, and QCISD(T) energies and scaled B3LYP/6-31G* ZPE corrections ($F=0.9614$)^[14] to those at B3LYP. The reported activation barriers refer to

transition states that were all relatively well described by a single Slater (Kohn–Sham) determinant and thus the single-reference methods applied were appropriate. For a more detailed discussion about electronic structures and possible diradicalic pathways see, for example, reference [15]. Details on the methodology and the used geometries are given in the Computational Methods section.

[4+2] Cycloaddition: The Diels–Alder reaction is an extremely powerful synthetic tool that has received a great deal of attention from theoreticians. Much effort has been devoted to mapping potential energy surfaces, such as the nature of the reaction pathway, that require an accurate determination of barrier heights and reaction energies. It is these we focus on in the present study.^[16] For that purpose, we chose a simple uniform set of [4+2] cycloaddition reactions in which first and second row elements are included. Recently, Sastry and co-workers^[17] benchmarked various quantum chemical methods for their performance on the



simple [4+2] cycloaddition shown in Equation (1). They concluded that the MP2 method is unsuitable for obtaining reliable energetics and that the B3LYP method appears to perform better, despite its apparent underestimation of reaction energies. We re-investigated the same series of reactions and find that the SCS-MP2 method outperforms both MP2 and B3LYP.

Activation and reaction energies for the reaction of ethylene with butadiene, cyclopentadiene, pyrrole (in *anti* (*a*) and *syn* (*s*) fashion), furan, silole, phosphole (in *anti* (*a*) and *syn* (*s*) fashion), and thiophene [Eq. (1)] are summarized in Table 1

Table 1. Reaction and activation energies [kcal mol⁻¹] for the Diels–Alder reactions of Equation (1).^[a,b,c]

X	Energy	HF		B3LYP		MP2		SCS-MP2		QCISD(T)	G3(OK) (T-corr. G3) ^[d]	Exptl
		S	S	L	S	L	S	L				
none	ΔE	-36.8	-36.9	-28.2	-47.0	-44.5	-43.1	-40.0	-40.5	-37.8(-38.4)	-38.7 ^[e]	
	ΔE^\ddagger	47.5	24.7	28.3	20.1	15.7	26.8	23.9	27.4	24.4(26.9)	27.5 ^[f]	
CH ₂	ΔE	-18.5	-18.6	-10.6	-32.0	-30.9	-28.2	-26.6	-25.2	-24.2 (-25.2)	-20.9 ^[g]	
	ΔE^\ddagger	42.0	22.2	25.9	13.6	9.4	20.5	17.6	21.9	18.8(19.8)	21.4 ^[h]	
NH <i>a</i>	ΔE	4.1	6.4	15.0	-3.7	-1.5	-2.7	-0.2	-2.4	0.1		
	ΔE^\ddagger	49.8	32.3	37.5	24.7	21.9	30.2	28.7	30.6	28.8		
NH <i>s</i> ^[i]	ΔE	1.8	4.5	16.7	-5.9	-3.4	-4.9	-2.0	-4.4	-1.7		
	ΔE^\ddagger	49.8	32.3	37.5	24.7	21.9	30.2	28.7	30.6	28.8		
O	ΔE	-6.8	-3.8	3.1	-13.6	-12.6	-12.0	-10.6	-11.1	-10.2		
	ΔE^\ddagger	44.4	27.0	30.9	20.0	15.9	26.1	23.4	26.7	23.7		
SiH ₂	ΔE	-15.8	-19.6	-12.7	-33.2	-32.9	-28.1	-26.9	-24.9	-25.2		
	ΔE^\ddagger	43.2	21.4	24.5	12.4	7.4	19.9	16.4	21.5	17.1		
PH <i>a</i>	ΔE	-15.3	-16.0	-7.8	-29.1	-28.0	-25.7	-23.9	-22.9	-21.7		
	ΔE^\ddagger	46.6	26.6	30.2	17.1	12.0	24.2	20.5	25.9	22.0		
PH <i>s</i>	ΔE	-13.0	-13.9	-5.8	-27.1	-26.0	-23.7	-22.0	-21.0	-19.9		
	ΔE^\ddagger	46.3	26.4	30.1	17.3	12.3	23.8	20.2	25.3	21.4		
S	ΔE	-2.7	-1.4	7.7	-11.7	-9.2	-10.2	-7.3	-8.7	-6.3		
	ΔE^\ddagger	54.7	35.9	40.3	27.4	23.0	33.4	30.5	34.5	31.3		
MAE		13.6	4.5	10.9	5.4	6.6	2.9	1.1	2.4	-		
MAX		26.1	6.5	18.4	9.2	10.0	5.3	2.4	4.4	-		

[a] S=6-31G*, L=6-311++G(3df,3pd). [b] B3LYP/6-31G* scaled ZPE included, others with HF-ZPEs. [c] MP2/6-31G* geometries except for those at HF and B3LYP. [d] In parentheses, exptl temperature corrected G3 energies (see Computational Methods). [e] References [18,19] (T)=849 K. [f] Reference [19] (T)=858 K. [g] Reference [20] (T)=547.75 K. [h] Reference [20] (T)=545.65 K. [i] No TS could be located for the *syn*-pyrrole cycloaddition.^[17]

for the HF, B3LYP, MP2, SCS-MP2, QCISD(T), and G3(0 K) levels of theory with the S and L basis sets. This table also gives the experimental reaction and Arrhenius activation energies for the cycloaddition of ethylene to butadiene and to cyclopentadiene, as well as the correspondingly temperature corrected G3 energies (see Computational Methods). The mean average (MAE) and maximum (MAX) errors of the combined activation and reaction energies calculated with these methods are referenced against G3(0 K) (which is expected to be accurate to about $0.5 \text{ kcal mol}^{-1}$ for the investigated systems) and are graphically depicted in Figure 1.

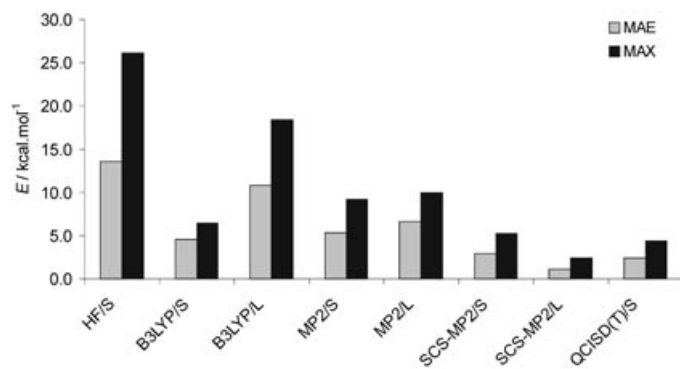


Figure 1. Mean average (MAE) and maximum (MAX) errors for the activation and reaction energies [kcal mol^{-1}] of the Diels–Alder reactions of Equation (1) with respect to the G3(0 K) energies.

The data reveal remarkable effects. Foremost, the performance of SCS-MP2 with the large 6-311++G(3df,3pd) basis set (L) is exceptionally good, as it hardly deviates from the G3 energies with an MAE of only $1.1 \text{ kcal mol}^{-1}$ for nine barriers and nine reaction energies, with the largest MAX being a mere $2.4 \text{ kcal mol}^{-1}$. With the smaller 6-31G* basis set (S) slightly larger differences are obtained, but with a performance that remains superior to MP2 (with either basis set) and also when compared to B3LYP. The common notion that relative energies improve with larger basis sets is not at all the case for either of these two methods. In fact, the MAE (MAX) values increase for MP2 from 5.4 (9.2) to 6.6 (10.0) kcal mol^{-1} in going from the smaller basis set S to the larger one L, while the corresponding MAE (MAX) value increases even more for B3LYP, from 4.5 (6.5) to 10.9 (18.4) kcal mol^{-1} , culminating in only a very modest improvement over HF/6-31G* (13.6 (26.1) kcal mol^{-1}). Clearly, SCS-MP2 outperforms either of these methods. As expected, the results with the smaller basis set are similar to the QCISD(T)/S data, while those with the larger set compare better with the G3 method, which also employs a large extended triple-zeta basis set for parts of the calculation. The agreement of the SCS-MP2 energies with the experimental activation and reaction energies for the cycloaddition of ethylene with both butadiene^[18,19] and cyclopentadiene^[20] is also good.

Instructive are the comparisons against G3 within each set of activation and reaction energies, which are displayed graphically for the calculations with the larger basis set L in Figures 2 and 3, respectively. This shows that the activation

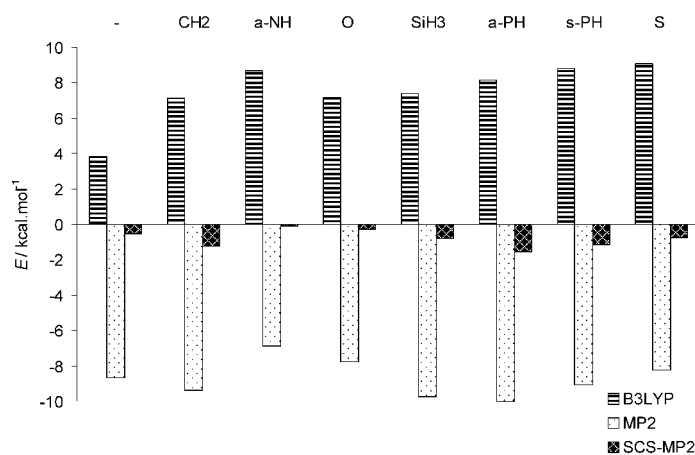


Figure 2. Deviations from G3(0 K) energies for the activation energies [kcal mol^{-1}] of the Diels–Alder reactions of Equation (1) using the 6-311++G(3df,3pd) basis set.

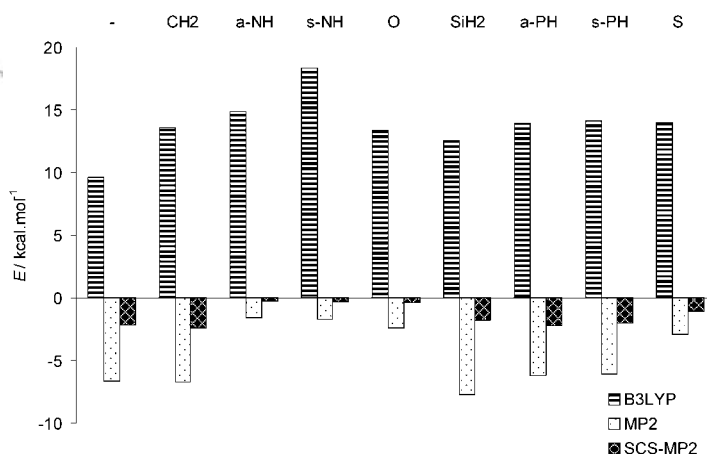


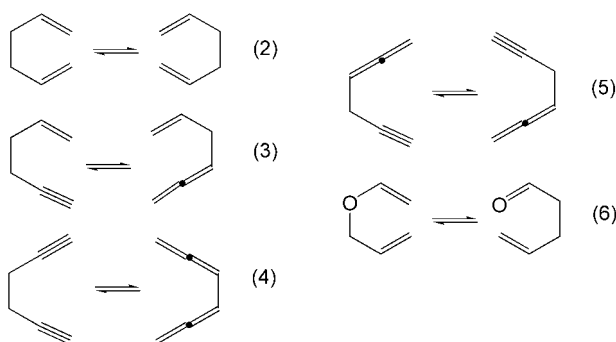
Figure 3. Deviations from G3(0 K) energies for the reaction energies [kcal mol^{-1}] of the Diels–Alder reactions of Equation (1) using the 6-311++G(3df,3pd) basis set.

energies are all substantially overestimated at B3LYP and equally underestimated at MP2 with MAE values of 7.5 and $8.7 \text{ kcal mol}^{-1}$, respectively (see Figure 2). Just the opposite is observed for the reaction energies, but with a still larger underestimation at B3LYP and a smaller overestimation at MP2 with MAE values of 13.8 and $4.7 \text{ kcal mol}^{-1}$, respectively (see Figure 3). The performance of B3LYP is rather dismal, as the ethylene cycloadditions to pyrrole, furan, and thiophene are even erroneously endothermic at this level of theory. This poor behaviour of B3LYP underscores the imbalanced treatment of π conjugation.^[7,8] In passing, we note that this method also occasionally has difficulties in correctly predicting the stereochemistry of Diels–Alder reactions.^[21] In conclusion, SCS-MP2 gives impressively good comparisons for both the activation and reaction energies with MAE values of only 0.8 and $1.4 \text{ kcal mol}^{-1}$, respectively, and performs far superior to both MP2 and B3LYP. Note that the two empirical parameters of the SCS-MP2 method have *not* been specially adjusted to reproduce activation barriers, which indicates that the scaling procedure has a deep physi-

cal basis and removes the inherent bias of the original MP2 method.

[3,3] Sigmatropic shifts: Another important class of pericyclic reactions is the sigmatropic shift.^[22] Of these we focus on the reaction energies and barriers for the Cope and Claisen rearrangements or [3,3] shifts, but again not on the nature of the reaction pathway as this aspect has already been discussed in the literature.^[23] In passing, we do note that all five MP2-optimized transition structures are dissymmetric. Importantly, the energies of the transition structures are not very sensitive to geometrical distortions (see Computational Methods).

As test set for the performance of SCS-MP2 we choose the set of four reactions, Equations (2)–(5), that Houk and co-workers^[15] reported on earlier, complemented with the parent Claisen rearrangement, Equation (6). The conclusion



of the earlier study was that the MP2 activation energies are unsatisfactory for the Cope rearrangements and that instead B3LYP performs better.^[15] We reinvestigated these reactions with SCS-MP2 in comparison to experimental activation and reaction energies and those obtained with the B3LYP, MP2, QCISD(T), and G3 methods, all of which are summarized in Table 2. Figure 4 graphically presents the mean average (MAE) and maximum (MAX) errors of the combined five activation and three reaction energies calcu-

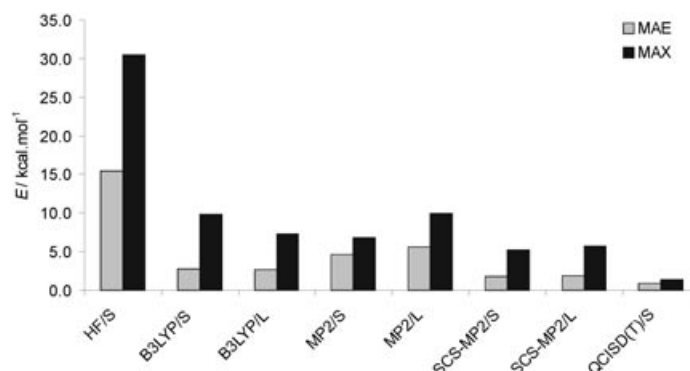


Figure 4. Mean average (MAE) and maximum (MAX) errors for the activation and reaction energies [kcal mol⁻¹] of the [3,3] sigmatropic shifts of Equations (2)–(6) with respect to the G3(0 K) energies.

lated with these methods and referenced against G3(0 K); the Cope rearrangements [Eqs. (2) and (5)] are degenerate processes. Comparisons of the deviation in B3LYP, MP2, and SCS-MP2 energies, obtained with basis set L, from those at G3 are graphically displayed in Figure 5.

SCS-MP2/L performs well, better than MP2, with a MAE of 1.9 kcal mol⁻¹, but not as well as for the Diels–Alder reac-

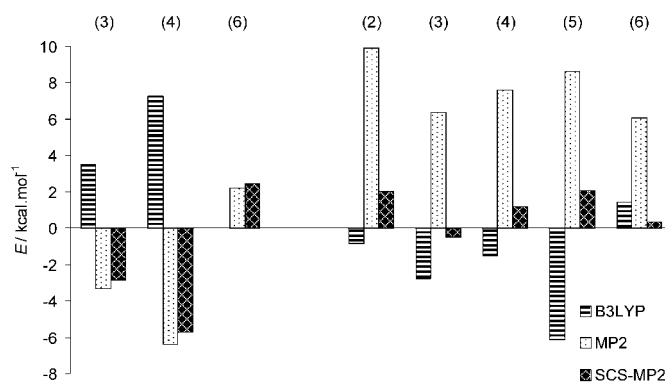


Figure 5. Deviations from G3(0 K) energies for reaction energies (left) and activation energies (right) [in kcal mol⁻¹] of the [3,3] sigmatropic shifts of Equations (2)–(6) using the 6-311++G(3df,3pd) basis set.

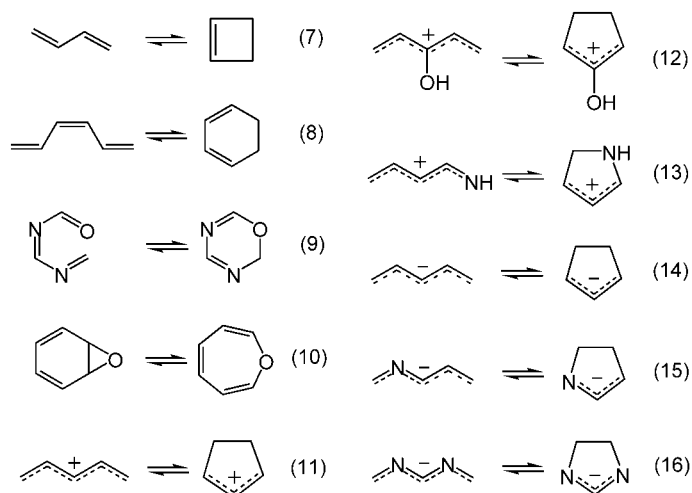
Table 2. Reaction and activation energies [kcal mol⁻¹] for the Cope rearrangements of Equations (2)–(5).^[a,b,c]

Eq.	Energy	HF	B3LYP		MP2		SCS-MP2		QCISD(T)	G3(OK)	Exptl
		S	S	L	S	L	S	L	S	(T-corr. G3) ^[d]	
(2)	ΔE^{\ddagger}	62.3	34.1	35.4	27.7	24.6	34.7	32.5	35.8	34.5 (34.5)	34.3 ^[e]
(3)	ΔE	0.2	-5.2	-4.3	2.4	2.6	2.0	2.1	-1.2	-0.7	
	ΔE^{\ddagger}	59.5	33.0	35.1	28.7	26.0	34.8	32.8	32.7	32.4 (32.6)	32.7 ^[f]
(4)	ΔE	-3.8	-15.4	-12.8	0.2	0.9	-0.3	0.2	-6.9	-5.5	
	ΔE^{\ddagger}	63.4	32.7	35.7	28.3	26.6	34.1	33.0	33.0	34.2 (34.6)	34.4 ^[g]
(5)	ΔE^{\ddagger}	60.3	33.7	36.0	23.7	21.2	29.5	27.7	29.8	29.8 (30.0)	30.8 ^[h]
(6)	ΔE	-20.4	-18.3	-16.6	-21.2	-18.8	-21.1	-19.0	-19.6	-16.6 (-16.2)	-17 ^[i]
	ΔE^{\ddagger}	47.5	27.8	28.5	24.8	23.9	30.1	29.6	30.2	30.0 (29.4)	30.3 ^[j]
	MAE	15.4	2.7	2.6	4.6	5.6	1.7	1.9	0.9	–	
	MAX	30.5	9.8	7.3	6.8	9.9	5.2	5.7	1.4	–	

[a] S=6-31G*, L=6-311++G(3df,3pd). [b] B3LYP/6-31G* scaled ZPE included, others with HF-ZPEs. [c] MP2/6-31G* geometries except for those at HF and B3LYP. [d] In parentheses, exp. temperature corrected G3 energies (see Computational Methods). [e] Reference [24] $\langle T \rangle = 530.8$ K. [f] Reference [25] $\langle T \rangle = 638.15$ K. [g] Reference [26] $\langle T \rangle = 551.65$ K. [h] Reference [27] $\langle T \rangle = 478.1$; experimental E_a is for 4-methyl-1,2-hexadien-5-yne. [i] Reference [28] $\langle T \rangle = 454.65$ K. [j] Reference [29] $\langle T \rangle = 454.65$ K.

tions as the MAX value of 5.7 kcal mol⁻¹ illustrates. Particularly, the reaction energies for the [3,3] shifts of Equations (3) and (4) show significant deviations (Figure 5). This behavior can be traced to the allene → propyne (C₃H₄) conversion, which is not well treated with either MP2 or B3LYP. In the original paper by one of us,^[9] it was shown that relative to QCISD(T) (ΔE = -1.5 kcal mol⁻¹), MP2 and SCS-MP2 give errors of 3.3 and 2.7 kcal mol⁻¹, respectively, (correctly favoring propyne) and B3LYP of -3.3 kcal mol⁻¹ (favoring allene). The same characteristics are observed for the reactions in Equations (3) and (4), which concern two propyne → allene conversions. For both cases the SCS-MP2 reaction energies are slightly better than those at MP2. The calculated exothermicity of the allyl vinyl ether/4-pentenal Claisen rearrangement is at the B3LYP level in perfect agreement with the G3(0 K) value, while both the MP2 and SCS-MP2 values are only slightly worse. The behavior of SCS-MP2 in calculating the activation energies for these electronically difficult to describe reactions is far better (Figure 5, right-hand side). With an MAE value of only 1.2 (0.6) kcal mol⁻¹, the SCS-MP2/L (S) energies resemble closer the G3 and experimental barriers of 30–34 kcal mol⁻¹ than either MP2 or B3LYP.

Electrocyclization reactions: Interconverting cyclic and acyclic compounds by electrocyclic processes represents another class of pericyclic reactions that is important to preparative organic chemistry.^[30] Besides the ubiquitous ring-opening and -closing reactions of neutral systems with an even number of participating atoms, there are also numerous examples of cations and anions with an odd number of participating atoms that undergo these reactions. Like the cycloadditions and sigmatropic rearrangements, many electrocyclizations are known in which a heteroatom is involved. The pericyclic nature of this reaction has been amply debated, but only those of the very polar, ylid-like systems show evidence for reactive intermediates.^[31] Again we focus only on activation and reaction energies. In this case, we chose sets of neutral molecules [Eqs. (7)–(10)], cations [Eqs. (11)–(13)], and anions [Eqs. (14)–(16)] to illustrate that SCS-MP2 performs well for a broad range of structures.



The set of neutral reactions consists of two parent systems, the heavily studied 4e electrocyclic ring opening of cyclobutene^[32,33] and the 6e ring closure of 1,3,5-hexatriene,^[34,35,36] and two reactions that contain heteroatoms, namely the ring closure of 1-oxa-3,5-diazahexatriene,^[37] which also illustrates ring-chain tautomerism, and the important oxepine–benzeneoxide interconversion.^[38] All these reactions have been well documented in the literature. The second set consists of three cations, the well-studied ring closure of the parent 4e pentadienyl cation,^[13,39,40,41] and its 3-hydroxy^[42,43] and 1-aza derivatives^[44] that received less attention, but that are of synthetic value for the preparation of cyclopentenones (Nazarov reaction) and pyrrole derivatives. The third group is composed of the 6π-electron pentadienyl anion,^[41,45] which does not cyclize,^[46] and its 2-aza^[47] and 2,4-diaza derivatives, which readily lead to the heterocyclic products.^[48] These processes are depicted in Equations (7)–(16), with the cyclized products shown on the right hand side. The activation and reaction energies for ring closure at HF, B3LYP, MP2, SCS-MP2, QCISD(T), and G3(0 K) for all ten reactions are summarized in Table 3, which also lists the experimental data for the ring-closure reactions of 1,3-butadiene, 1,3,5-hexatriene, and oxepine. The table further gives the MAE and MAX values for the differences of these methods with respect to G3, which are also graphically presented in Figure 6 for clarity.

The ring opening of cyclobutene to 1,3-butadiene has received much attention. The reaction is exothermic by 10.9 kcal mol⁻¹ and has an activation energy of 34.5 ± 0.5 kcal mol⁻¹ (Arrhenius E_a = 32.9 ± 0.5), both of which compare well with the G3(0 K) calculated reaction and activation energies of 13.4 and 32.4 kcal mol⁻¹, respectively; note that the entry in Table 3 gives the data for the ring closure reaction (45.4 kcal mol⁻¹). Likewise, the G3(0 K) activation energy of 30.8 kcal mol⁻¹ for the hexatriene–cyclohexadiene ring-closure reaction is in good agreement with the reported experimental value of 29 kcal mol⁻¹. We assume that G3 performs equally well for the other reactions.

For the benzeneoxide–oxepine system the presence of both tautomers in solutions at low and room temperature has been reported.^[49,50] The quantum chemical methods considered here give relative energies from -3 to 3 kcal mol⁻¹, with small negative values for the MP2-methods and small positive ones for QCISD(T) and G3. This is in reasonable agreement with the experimentally determined reaction enthalpy of -1.5 to -1.9 kcal mol⁻¹, which, however, must be corrected for solvent effects when detailed comparisons between theory and experiment are made; the dipole moment for benzeneoxide is about 0.6 Debye larger than that of the tautomer. Again, SCS-MP2 improves the MP2 result significantly by about 2 kcal mol⁻¹. The calculated barrier of about 6.6 kcal mol⁻¹ (G3, E_a (exp) = 7.2–9.1 kcal mol⁻¹) is well reproduced by the SCS-MP2, QCISD(T) and DFT calculations, but strongly underestimated by the MP2 method.

The cyclization of the pentadienyl cations [Eqs. (11)–(13)] shows the same trend as found for the neutral compounds [Eqs. (7)–(10)], but for the pentadienyl anions [Eqs. (14)–(16)] the particularly poor performance of B3LYP stands out. Heats of reaction are generally overestimated by about

Table 3. Reaction and activation energies [kcal mol⁻¹] for the electrocyclization reactions in Equations (7)–(16).^[a,b,c]

Eq.	Energy	HF		B3LYP		MP2		SCS-MP2		QCISD(T)	G3(OK)	Exptl
		S	S	L	L	S	L	S	L	S		
(7)	ΔE	13.5	12.7	16.1	8.7	10.1	9.7	11.3	11.5	13.4	10.9 ^[d]	
	ΔE^\ddagger	58.9	46.7	47.5	44.7	42.8	47.6	46.2	46.6	45.8	45.4 ^[d,e]	
(8)	ΔE	-14.9	-12.6	-9.3	-19.5	-17.9	-18.2	-16.0	-16.4	-14.4		
	ΔE^\ddagger	45.9	30.3	31.1	26.7	24.4	30.9	30.4	32.1	30.8	29 ^[f]	
(9)	ΔE	-7.1	-6.3	-3.6	-7.3	-8.1	-6.0	-6.4	-6.3	-7.0		
	ΔE^\ddagger	17.0	9.0	10.5	12.5	11.6	15.0	14.8	12.8	11.6		
(10)	ΔE	-36.4	1.2	3.1	-3.1	-2.0	-1.7	-0.7	0.1	0.9	1.5 ^[g]	
	ΔE^\ddagger	16.5	6.4	7.5	2.1	1.6	6.3	6.5	7.4	6.6	7.5 ^[h]	
(11)	ΔE	-15.4	-15.0	-13.2	-19.6	-19.4	-18.1	-17.0	-17.8	-17.3		
	ΔE^\ddagger	22.2	13.2	13.2	7.7	6.3	7.6	9.5	10.1	9.6		
(12)	ΔE	1.9	-1.9	-0.9	-4.3	-5.4	-3.0	-3.2	-2.3	-3.2		
	ΔE^\ddagger	31.6	19.9	19.8	14.9	11.2	17.5	16.8	19.7	18.1		
(13)	ΔE	-50.1	-53.0	-52.1	-60.8	-62.0	-58.8	-57.9	-56.8	-58.4		
	ΔE^\ddagger	10.3	12.5	11.6	11.2	10.3	10.8	10.0	10.8	10.2		
(14)	ΔE	15.2	16.8	17.8	6.8	6.7	8.5	8.3	9.0	9.6		
	ΔE^\ddagger	53.0	41.5	42.1	33.9	32.7	36.6	36.2	36.6	36.6		
(15)	ΔE	-6.9	1.1	3.2	-10.0	-8.7	-9.2	-8.1	-7.9	-6.7		
	ΔE^\ddagger	36.6	29.1	29.6	20.0	18.7	23.8	21.8	23.3	22.9		
(16)	ΔE	-33.2	-17.9	-14.6	-29.9	-26.3	-31.3	-27.1	-28.3	-25.3		
	ΔE^\ddagger	25.3	19.4	18.9	9.7	7.2	11.4	9.6	13.2	11.1		
MAE		9.0	3.3	4.3	2.7	3.1	1.6	1.0	1.1	-		
MAX		37.4	8.2	10.7	5.1	6.9	6.0	3.2	2.9	-		

[a] S=6-31G*, L=6-311++G(3df,3pd). [b] B3LYP/6-31G* scaled ZPE included, others with HF-ZPEs. [c] MP2/6-31G* geometries except for those at HF and B3LYP. [d] Reference [33]. [e] The ΔH^\ddagger for the cyclobutene ring-opening reaction is 34.5 kcal mol⁻¹. [f] References [35,36]. [g] Reference [49]. [h] Reference [50].

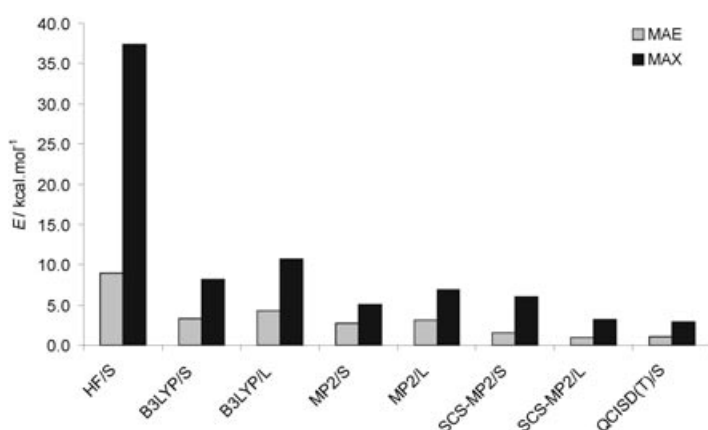


Figure 6. Mean average (MAE) and maximum (MAX) errors for the activation and reaction energies [kcal mol⁻¹] of the electrocyclization of Equations (7)–(16) with respect to G3(0 K) energies.

7–11 kcal mol⁻¹ and reaction barriers by about 5–8 kcal mol⁻¹.

The MAE and MAX values for the combined ten activation and ten reaction energies of only 1.0 and 3.2 kcal mol⁻¹, respectively, show that the performance of SCS-MP2 with the larger basis set is excellent. The errors are slightly larger with the smaller basis set, mainly due to the 6.0 kcal mol⁻¹ larger cyclization energy for the 2,4-diazapentadienyl anion than at G3. Both MP2 and B3LYP show the opposite behavior, that is, the MAE and MAX values increase with the larger basis set. Both these methods perform poorer than SCS-MP2 with B3LYP giving the least satisfactory energies. The HF/S energies in Figure 6 nicely illustrate for the elec-

trocyclizations, even more so than for the [3,3] shifts and the Diels–Alder reactions, that inclusion of the effects of electron correlation are of imminent importance; the MAE and MAX values of 9.0 and 37.4 kcal mol⁻¹, respectively, are very substantial.

The performance of SCS-MP2 over both MP2 and B3LYP is even much better than indicated by the MAE and MAX values when the activation and reaction energies are separated as shown graphically in Figures 7 and 8 for the data obtained with the larger basis set. At MP2/L the reaction energies are overestimated and the activation energies are underestimated, while the opposite is the case at B3LYP where this effect is even enhanced. This is not at all the case for SCS-MP2. Only the activation energy for the cyclization

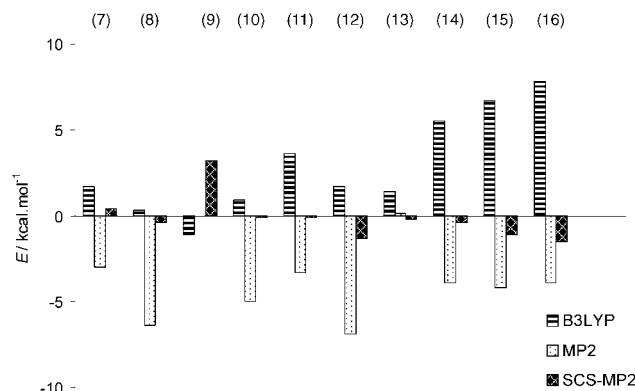


Figure 7. Deviations from G3(0 K) energies [in kcal mol⁻¹] of the electrocyclizations of Equations (7)–(16) using the 6-311++G(3df,3pd) basis set.

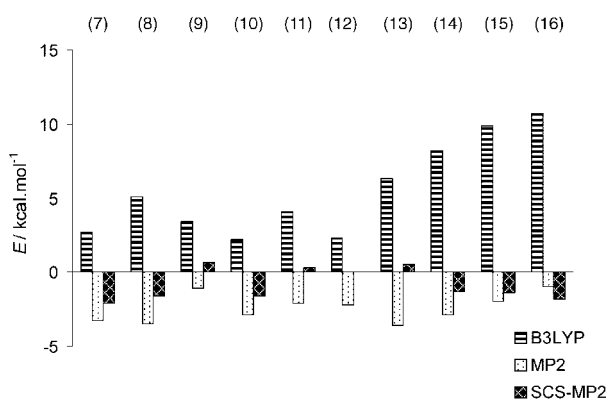


Figure 8. Deviations from G3(0 K) energies for the reaction energies [in kcal mol⁻¹] of the electrocyclizations of Equations (7)–(16) using the 6-311++G(3df,3pd) basis set.

of 1-oxo-3,5-diazahexatriene to 1-oxa-3,5-diazine deviates with a “large” difference of 3.2 kcal mol⁻¹ from the G3 energy barrier.

Conclusion

Spin-component-scaled MP2 (SCS-MP2) calculations represent a considerable improvement over traditional MP2 calculations, even for very basic organic reactions, such as the pericyclic reactions we consider here. Where MP2 considerably underestimates activation barriers for [4+2] cycloadditions [Diels–Alder reactions, Eq. (1)], [3,3] sigmatropic rearrangements [Eqs. (2)–(6)], and electrocyclization reactions [Eqs. (7)–(16)], SCS-MP2 energies are in harmony with G3, QCISD(T) and, where available, experimental values. Although B3LYP has proven to be a fast and accurate tool for computational organic chemistry, it occasionally does not perform well. We suggest SCS-MP2 as a very attractive alternative. Especially for Diels–Alders reactions, the accurate B3LYP activation barriers that are obtained only with a small basis set may be coincidental as the reaction energies are generally too low. Instead, SCS-MP2 predicts both accurate activation and accurate reaction energies.

Computational Methods

All calculations were performed with the Gaussian 98 suite of programs.^[51] All reported HF, MP2(full), SCS-MP2(full) and B3LYP/6-31G* energies (in kcal mol⁻¹) are obtained by using geometries optimized at the same level of theory, but with the 6-31G* basis set (S), except for both the B3LYP/L energies of the electrocyclization reactions (Table 3) that are based on the geometries optimized at this level with the 6-311++G(3df,3pd) basis set (L) and the single-point QCISD(T)/S//MP2(full)/S energies that are extracted from the G3 calculations. SCS-MP2 single-point energies, using MP2/S optimized geometries, are obtained by scaling the α - α and β - β components of the second-order perturbation energies by 1/3 and the α - β components by 6/5.^[9] For the HF, MP2, SCS-MP2 and QCISD(T) methods we included zero-point energies (ZPE) from scaled HF/S-frequencies ($F=0.8929$), while for the B3LYP-methods scaled B3LYP/S-frequencies ($F=0.9614$) were used.^[14] Only the G3 energies are, where appropriate, compared with experimental data at the experimen-

tally applied temperatures to check their temperature dependence (see values in parentheses in Tables 1 and 2). For that purpose, we added for comparison, Arrhenius energies of activation, a thermal correction from scaled HF/S-frequencies and the RT term to the calculated G3 energy using the temperature at the midpoint of the experimental range, that is, $E^{\ddagger} = E^{\ddagger} + RT = E^{\ddagger}_{(G3^*)} + \Delta E_{\text{therm.corr.}} + RT$, in which $E_{(G3^*)}$ is the electronic energy without the ZPE correction. The same approach was applied to the reaction energies, that is, $E_r = E_{r(G3^*)} + \Delta E_{\text{therm.corr.}}$

[3,3] Sigmatropic transition structures can be sensitive to the theoretical method employed as illustrated in a recent study by Birney.^[52] They are usually tighter at MP2, displaying 1,4-diyli character,^[23] than they are at B3LYP (and HF) with differences in C–C bond breaking/forming distances that can be over 0.1 Å. However, these geometrical differences appear to have little influence on the energies of the transition structures of the pericyclic reactions of this study. Illustrative is the Cope rearrangement [Eq. (2)]. The C_{2v} -symmetric structure is a transition structure at B3LYP, but an intermediate at MP2/S,^[53] while its associated transition state is dissymmetric with C–C bond-breaking/forming lengths of 1.761 and 1.814 Å, indicating an asynchronous diradicaloid pathway; no open shell singlet states were located. However, the difference in activation energy between MP2/L//B3LYP and MP2/L//MP2/S is only 1.0 kcal mol⁻¹ and at SCS-MP2/L even smaller (0.8 kcal mol⁻¹). For consistency, we do not mix theoretical levels in this study, but it is evident that the less expensive MP2//B3LYP approach is a viable option for determining activation energies.

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