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Correlation Effects on Semiempirical Transition States

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Abstract: MNDOC calculations with use of perturbation and configuration interaction techniques for electron correlation are reported for 24 reactions of simple organic molecules. The correlation effects on activation energies and transition structures are discussed and compared with the available ab initio data. The numerical results provide some general guidelines for semiempirical MNDOC studies of thermal organic reactions.

(I) Introduction

A recent comparison between semiempirical and ab initio transition states has shown[1] that MNDO[2] and MNDOC[3] usually reproduce the qualitative features of state-of-the-art ab initio potential surfaces and transition structures. At the SCF level, satisfactory agreement was generally found for the geometries, frequencies, and zero-point vibrational energies of transition states, and the correlated MNDOC barriers were normally realistic enough to allow correct mechanistic conclusions.

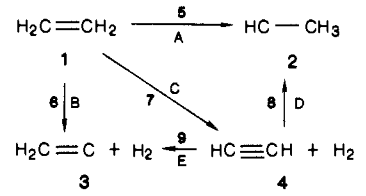
In our previous paper,[1] electron correlation was treated explicitly by second-order BWEN perturbation theory only when evaluating the correlated MNDOC energies at optimized MNDOC SCF geometries.[3] The present paper investigates correlation effects on MNDOC transition states in greater depth, by using more refined treatments of electron correlation and by optimizing transition structures at the correlated level. It is our main objective to study the importance of electron correlation for semiempirical transition states in a systematic manner and to suggest some guidelines for such semiempirical calculations. Ab initio reference data on correlation effects are included when available, to allow qualitative comparisons with the semiempirical results.

(II) Semiempirical Calculations

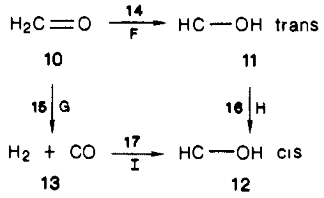
According to the general philosophy of the MNODC approach,[3-5] the exact MNDOC correlation energy (full-CI) should be approximated as closely and efficiently as possible. For this purpose, we may use three correlation treatments:[3-5] Second-order Brillouin-Wigner perturbation theory with Epstein-Nesbet energy denominators (BWEN), configuration interaction with all singly and doubly excited configurations (DECI), or a CI perturbation treatment (PERTCI).[6] BWEN is the fastest and least accurate of these methods, while DECI is the slowest and most accurate one. For the sake of efficiency, MNDOC calculations normally treat electron correlation by BWEN.[1,3] To check whether this is sufficiently accurate for transition structures, the present paper also reports the corresponding PERTCI and DECI energies as well as the optimized PERTCI geometries.

Some details of the present calculations need to be specified: The closed-shell SCF determinant Ψ_0 is always taken to be the only main configuration. In the PERTCI calculations, a doubly excited configuration Ψ_k is selected to belong to the set of strongly coupled configurations if its interaction $|H_{k0}|^2(E_k - E_0)^{-1}$ with the SCF determinant Ψ_0 exceeds a threshold value T (matrix element H_{k0}, configuration energies E_k and E_0). Diagonalization of the CI matrix for these selected configurations yields the SELCI energy, while the PERTCI energy is obtained by adding the contributions from the remaining configurations as evaluated by second-order BWEN perturbation theory.[6] In our present PERTCI calculations, the threshold parameter is set to $T = 0.01$ eV because optimized PERTCI transition structures are then very close to the corresponding DECI structures, with typical deviations of only 0.001 Å in bond lengths and 0.1° in bond angles (see supplementary material for the convergence behavior with respect to the choice of T). For $T = 0.01$ eV, the number of selected configurations is usually less than 10% of the total number so that

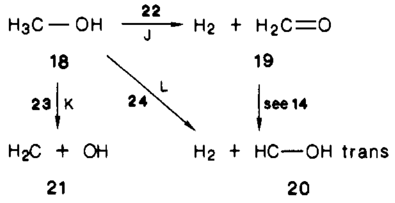
Scheme I. C_2H_4 Potential Surface



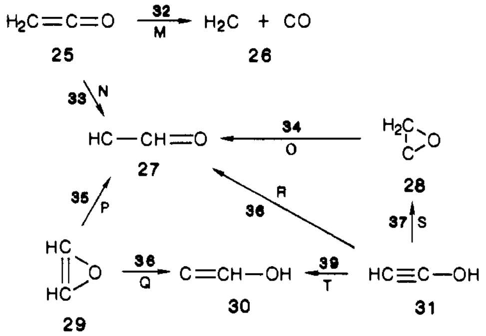
Scheme II. CH_2O Potential Surface



Scheme III. CH_3OH Potential Surface



Scheme IV. C_2H_2O Potential Surface



Scheme V. Other Reactions

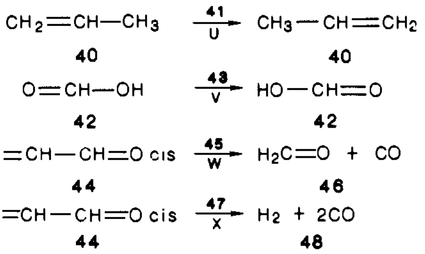


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Table I. MNDOC Relative Energies (kcal/mol) for **1–39**

		SCF geometry				BWEN geometry		PERTCI geometry	
system		SCF	BWEN	PERTCI	DECI	SCF	BWEN	SCF	PERTCI
C_2H_4	**1**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	2	57.6	58.9	59.7	59.6	57.3	59.2	57.3	59.8
	3	91.3	86.2	87.9	88.2	91.4	86.1	91.3	87.8
	4	45.1	40.7	42.0	42.6	45.7	40.2	45.3	41.7
	5	81.4	78.7	79.8	79.5	80.9	79.3	81.0	80.4
	6	109.2	100.4	101.4	101.5	109.4	100.1	109.4	101.2
	7	150.7	140.3	143.1	142.6	153.3	138.0	153.3	141.2
	8	124.1	113.2	114.3	113.8	123.1	114.4	123.2	115.1
	9	115.3	105.4	108.5	108.6	115.4	105.3	115.3	108.7
CH_2O	**10**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	11	31.1	33.6	33.5	33.2	30.9	33.8	31.0	33.6
	12	31.6	32.1	32.1	31.7	31.5	52.3	31.5	32.1
	13	10.5	5.9	7.8	8.1	10.8	5.7	10.6	7.7
	14	103.9	93.3	96.8	96.6	103.8	93.4	103.9	96.8
	15	83.1	71.3	73.1	73.2	83.1	71.3	83.3	72.8
	16	53.8	56.5	55.7	56.0	53.6	56.7	53.7	55.9
	17	137.4	125.5	129.2	129.1	138.7	125.3	137.8	128.8
CH_3OH	**18**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	19	29.9	20.3	21.8	22.4	30.2	20.0	30.1	21.6
	20	61.1	53.8	55.3	55.7	61.1	53.8	61.1	55.2
	21	89.9	84.2	85.4	86.2	89.9	84.2	89.9	85.4
	22	139.8	128.4	129.0	129.4	141.4	127.3	141.4	127.4
	23	96.1	90.9	91.8	92.6	96.1	90.8	96.1	91.8
	24	93.4	82.7	83.1	83.5	94.6	81.3	95.0	81.9
C_2H_2O	**25**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	26	78.0	75.3	76.8	77.5	78.1	75.2	77.9	76.8
	27	61.0	64.5	62.7	62.7	60.9	64.6	60.9	62.8
	28	51.0	55.3	53.8	53.8	50.9	55.4	50.9	53.9
	29	69.8	75.8	72.3	72.2	70.0	75.6	70.0	72.1
	30	67.4	72.3	69.8	69.7	67.5	72.2	67.5	69.7
	31	15.9	21.9	20.1	20.7	16.4	21.4	16.1	19.9
	32	78.3	76.9	78.0	78.8	78.4	77.7	78.3	78.1
	33	69.5	66.2	66.3	66.5	68.1	67.6	68.7	66.9
	34	121.5	119.2	119.0	119.3	121.4	119.4	121.4	119.1
	35	93.5	84.8	87.7	87.0	93.5	83.2	93.7	86.4
	36	127.2	105.7	110.9	110.6	137.7	110.7	137.3	118.0
	37	138.5	126.5	129.5	130.1	135.6	129.1	137.0	130.7
	38	138.5	123.8	127.8	127.9	137.1	123.4	138.4	127.3
	39	78.1	78.5	78.0	78.0	78.0	77.4	78.0	77.4

PERTCI is considerably faster than DECI.

All present calculations were carried out by using the standard MNDOC parameters.[3] All geometries were completely optimized by employing the Davidon–Fletcher–Powell algorithm[7] for minima and gradient norm minimization[8,9] for transition states. Technical details of the optimizations have been described elsewhere.[10]

(III) Results

As in our previous paper,[1] we study a set of 24 thermal organic reactions on the potential surfaces of ethylene, formaldehyde, methanol, ketene, propene, formic acid, and glyoxal. Schemes I–V show the investigated reactions which are denoted by capital letters whereas the minima and transition states involved are identified by boldface numbers. The selected set includes six [1,2]- and two [1,3]-sigmatropic hydrogen shifts, five other intramolecular rearrangements, four 1,1 and three 1,2 eliminations of H_2, and four other dissociation reactions.

The transition structures are defined in Figure 1 and in the supplementary material which contains the optimized MNDOC–SCF, BWEN, and PERTCI geometries for all transition states studied, along with the MNDOC DECI geometries for **14**–**17**. Table I lists the relative energies for the species **1**–**39** obtained from MNDOC heats of formation. Table II gives the MNDOC activation energies for all reactions studied (barrier heights for the endothermic reactions without zero-point corrections). The correlation effects on the MNDOC activation energies are summarized in Table III and compared to the best available ab initio data.[11-16] The most important correlation-induced changes in the optimized transition structures are listed in Table IV which includes all cases where the absolute difference between the MNDOC–SCF and PERTCI results exceeds 0.05 Å for bond lengths, 5° for bond angles, and 10° for dihedral angles; Table IV also contains some ab initio reference data[11] (geometry differences between RHF/6-31G* and MP2/6-31G*) and some information on the electronic structure of the MNDOC transition states. Finally, Table V gives a statistical evaluation of the correlation effects on the optimized MNDOC transition structures.

Before discussing our results, a remark on the accuracy of the ab initio data in Tables III and IV seems appropriate. Ab initio correlation effects naturally depend on the basis set and the correlation treatment used. This dependence has been studied carefully for reactions F and G on the formaldehyde surface:[13]

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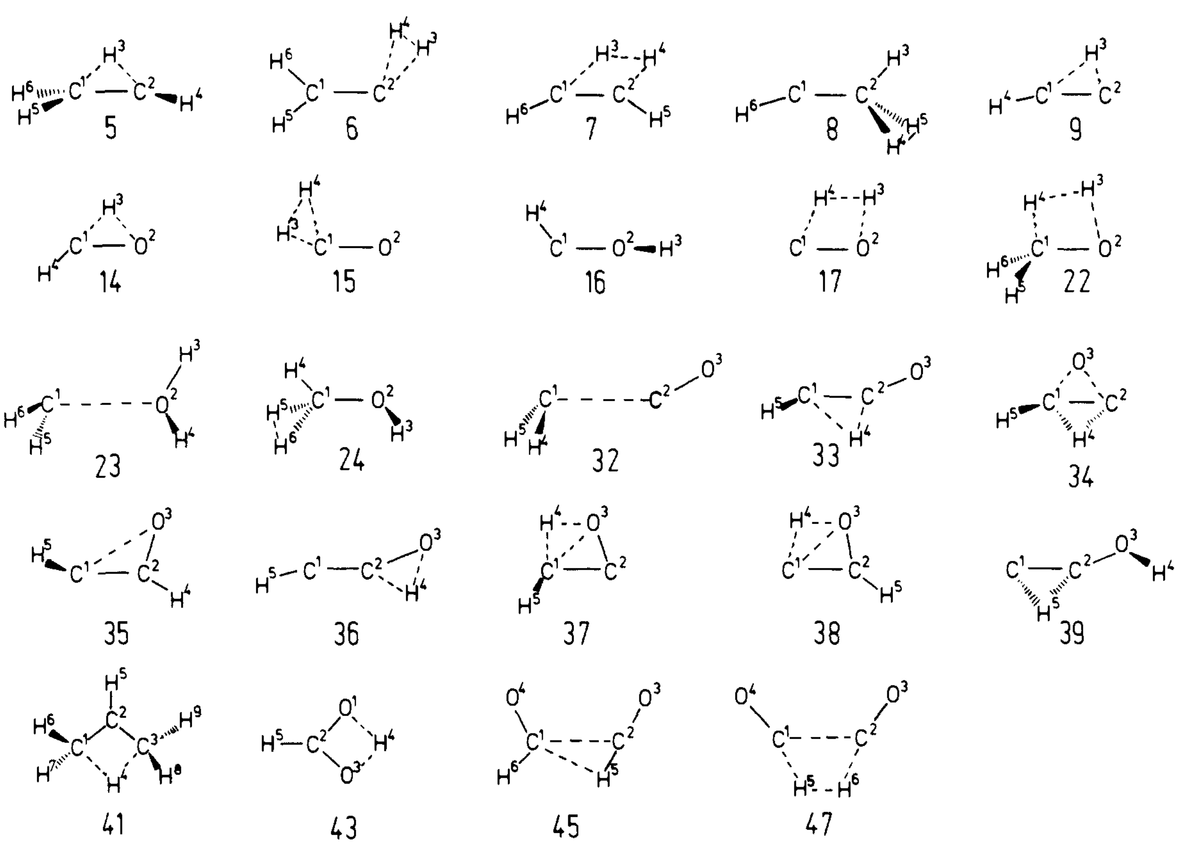

Figure 1. Definition of transition structures.

Table II. MNDOC Activation Energies (kcal/mol)[a]

	SCF geometry				BWEN geometry		PERTCI geometry	
reaction	SCF	BWEN	PERTCI	DECI	SCF	BWEN	SCF	PERTCI
A	81.4	78.7	79.8	79.5	80.9	79.3	81.0	80.4
B	109.2	100.4	101.4	101.5	109.4	100.1	109.4	101.2
C	150.7	140.3	143.1	142.6	153.3	138.0	153.3	141.2
D	79.0	72.6	72.4	71.2	77.5	74.2	77.9	75.2
E	70.2	64.7	66.5	66.0	69.8	65.1	69.9	67.0
F	103.9	93.3	96.8	96.6	103.8	93.4	103.9	96.8
G	83.1	71.3	73.1	73.2	83.1	71.3	83.3	72.8
H	22.7	23.0	22.2	22.8	22.7	23.0	22.7	22.3
I	126.9	119.6	121.5	121.1	128.0	119.6	127.2	121.1
J	139.8	128.4	129.0	129.4	141.4	127.3	141.4	127.4
K	96.1	90.9	91.8	92.6	96.1	90.8	96.1	91.8
L	93.4	82.7	83.1	83.5	94.6	81.3	95.0	81.9
M	78.3	76.9	78.0	78.8	78.4	77.7	78.3	78.1
N	69.5	66.2	66.3	66.5	68.1	67.6	68.7	66.9
O	70.5	63.9	65.2	65.4	70.5	64.0	70.5	65.2
P	23.7	9.1	15.3	14.8	23.4	7.7	23.7	14.3
Q	68.7	48.1	55.4	55.7	67.1	47.8	68.4	55.2
R	111.3	83.8	90.8	89.8	121.2	89.3	121.2	98.1
S	122.6	104.6	109.3	109.3	119.1	107.8	120.9	110.8
T	62.2	56.6	57.8	57.3	61.6	56.0	61.9	57.5
U	98.5	88.4	89.3	89.4	98.8	88.2	98.9	89.0
V	76.5	66.7	69.5	69.9	76.8	66.3	76.6	69.5
W	85.9	73.6	75.9	76.4	86.2	73.3	86.2	75.7
X	81.8	65.4	69.5	69.9	82.3	64.9	82.0	69.4

[a] On the basis of data in Table I.

For a sample of 20 basis sets, the difference between the RHF and MP4 activation energies was found to vary in the range 9.1–13.4 kcal/mol (F) and 15.0–23.0 kcal/mol (G); for the largest basis set, the computed correlation effect on the barrier was strongly influenced by the choice of the correlation treatment (MP2, MP3, MP4), being in the range 7.7–12.8 kcal/mol (F) and 9.6–15.9 kcal/mol (G) where the lowest value corresponds to MP3 and the highest one to MP4. Judging from the published material,[11,13,17] we may expect in Table III an accuracy of ±1 kcal/mol for the ab initio data for F and G but an appreciably lower accuracy for the remaining ab initio data; in particular, the MP3 values given for I and N–T may well be too low[18] (see also footnote *j* of Table III). With regard to optimized transition structures, it is still harder to estimate the accuracy of the published ab initio correlation effects[11,12,17] (see Table IV). In the most carefully studied case,[17] i.e., transition structure **15** for reaction G, the largest correlation effects are associated with the HH distance which, at the DZP level, is increased by values

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[18] At the 6-31G* level, the correlation effects on the barriers for reactions A–H are also almost always smaller for MP3 than for MP4 (ref 11).

Table III. Correlation Effects on Activation Energies (kcal/mol)[a]

	MNDOC[b]			ab initio	
reaction	BWEN	PERTCI	DECI	BEST	ref
A	2.7	1.7	2.0	1.6	*c*
B	8.7	7.7	7.7	8.4	*d*
C	10.5	7.6	8.1	6.4	*d*
D	6.4	6.6	7.8	0.0	*d, e*
E	5.5	3.7	4.2	0.7	*d*
F	10.7	7.2	7.4	12.8	*f*
G	11.8	10.0	9.9	15.9	*f*
H	−0.3	0.5	−0.1	−3.8	*d*
I	7.3	5.4	5.8	4.1	*g*
J	11.4	10.8	10.4	10.8	*c*
K	5.2	4.3	3.5		
L	10.8	10.3	9.9	5.6	*h*
M	1.4	0.3	−0.5		
N	3.3	3.2	3.0	−1.4	*i*
O	6.6	5.3	5.1	6.1	*i*
P	14.6	8.4	8.9	−4.5	*i, j*
Q	20.6	13.3	13.1	10.9	*i, j*
R	27.6	20.6	21.5	15.8	*i, j*
S	18.0	13.3	13.3	7.5	*i, j*
T	5.6	4.4	4.9	1.0	*i*
U	10.1	9.2	9.2	10.6	*k*
V	9.8	7.0	6.6	9.3	*k*
W	12.3	10.0	9.6		
X	16.4	12.3	11.9	11.6	*l*

[a] Differences between SCF and correlated values for the activation energies, evaluated at optimized SCF geometries (unless noted otherwise). [b] On the basis of the data in Table II. [c] Reference 11, MP4/6-311G** at RHF/6-31G* geometries. [d] Reference 11, MP4/6-31G* at RHF/6-31G* geometries. [e] Reference 11, MP3/6-31G** at RHF/6-31G* geometries yields 2.8 kcal/mol. [f] Reference 13, MP4/6-311++G(3df,3pd) at MP2/6-31G* geometries. [g] Reference 11, MP3/6-31G* at RHF/6-31G* geometries. [h] Reference 12, MP4SDQ/6-31G** at RHF/6-31G* geometries. [i] Reference 14, MP3/6-31G** at RHF/4-31G geometries. [j] Reference 14, MP2/6-31G** at RHF/4-31G geometries yields 2.0 (P), 17.8 (Q), 27.4 (R), and 10.0 (S) kcal/mol. [k] Reference 15, CEPA/DZP at RHF/4-31G geometries. [l] Reference 16, DECI/3-21G at RHF/3-21G geometries.

between 0.005 and 0.163 Å depending on the correlation treatment used, the best value being probably 0.093 Å. In view of this situation, we have decided to include in Table IV the largest consistent set of ab initio data available to us[11] (RHF/6-31G* vs. MP2/6-31G*) even though some of these data might not be the most accurate ones. We conclude from the preceding remarks that a comparison between semiempirical and ab initio correlation effects in Tables III and IV should focus more on qualitative trends than on quantitative aspects.

(IV) Discussion

We first address the question whether an explicit treatment of electron correlation is necessary at all in the semiempirical calculation of activation energies (using SCF optimized geometries, for the sake of simplicity). This question has basically been answered already in our previous study[1] which showed that the best correlated ab initio barriers for our selected set of reactions were reproduced much better by MNDOC–BWEN than by MNDO–SCF, the mean absolute deviations[19] being 9.0 and 21.5 kcal/mol, respectively. Hence, if we accept the best correlated ab initio results as reliable reference data, we must conclude that the explicit inclusion of electron correlation in the MNDOC formalism helps to improve the calculated activation energies.

According to Tables I–III, correlation effects almost always lower the calculated barriers. At the SCF optimized geometries, the average decrease amounts to 9.9 kcal/mol for MNDOC–BWEN, 7.6 kcal/mol for MNDOC–PERTCI, and 7.7 kcal/mol for MNDOC–DECI. Moreover, these decreases are not uniform ranging between 0 and more than 20 kcal/mol (see Table III). In order to avoid errors of this order of magnitude, it thus seems advisable to treat correlation effects explicitly also in the semiempirical calculation of activation energies.

At first sight, this recommendation runs counter to the argument that semiempirical methods such as MNDO account for electron correlation, in an average sense, by the semiempirical reduction of the two-electron integrals and by the parametrization. This argument is certainly valid for stable ground-state molecules, as can be shown, e.g., by comparing MNDO and MNDOC results for such molecules.[3] In transition states, however, where bonds are being broken and formed, it is reasonable to assume that the correlation effects are somewhat larger than in stable ground-state molecules; according to our present numerical evidence, this "extra" correlation is typically of the order of 10 kcal/mol, in a semiempirical MNDO-type framework, at least for the types of reactions studied presently. This "extra" correlation is not taken into account in MNDO–SCF calculations of transition states which consequently tend to overestimate the barriers.[1]

Inspection of Tables II and III shows that the BWEN approach usually exaggerates the correlation effects on energies by about 20% when compared with PERTCI or DECI, while the latter two methods are always very close to each other in their predictions (mean absolute deviation of 0.4 kcal/mol). In practice, it would seem sufficient to compute the correlation corrections to activation energies by BWEN as long as they are below 10 kcal/mol; if these corrections are larger, they should preferably be determined by PERTCI.

According to the data in Table III, the semiempirical and ab initio correlation effects on activation energies are usually of the same sign and usually assume large values for the same reactions so that there are qualitative similarities. In view of the remarks in section III, a more quantitative comparison is not feasible.

Having discussed energies at SCF optimized geometries up to this point, we now turn to the results at BWEN or PERTCI optimized geometries. As can be seen from Table II, the activation energies change only very slightly when using correlated instead of SCF optimized geometries. There is only one case (reaction R) where this change is larger than 4 kcal/mol, and the mean absolute change is 0.9 kcal/mol both for MNDOC–BWEN and MNDOC–PERTCI. It is thus justified in most cases to use MNDOC–SCF geometries for the evaluation of BWEN or PERTCI activation energies. This is very fortunate computationally because geometry optimizations are much faster at the SCF level than at the correlated level.

Looking at the optimized MNDOC-SCF, BWEN, and PERTCI geometries of individual transition states (see supplementary material) and at the corresponding statistical evaluation (see Table V), we find that the correlation-induced geometry changes are generally quite small. The largest of these geometry changes are listed in Table IV (see footnote *a*); they range up to 0.18 Å for bond lengths, up to 19° for bond angles, and up to 10° for dihedral angles, in absolute value. In order to find out when such large geometry changes may be expected, the contribution c_0^2 of the SCF determinant to the BWEN wave function and the number of important excited configurations with $|H_{k0}|^2(E_k - E_0)^{-1} > 0.2$ eV (both evaluated at the SCF optimized geometry) are also given in Table IV. As expected, large geometry changes correlate with low c_0^2 values (6 out of 8 transition states with $c_0^2 < 0.92$ appear in Table IV); likewise, if there are important excited configurations of class A where all MOs involved in the excitation have the same symmetry as the reaction coordinate, large correlation-induced geometry changes are probable (9 out of 11 such transition states appear in Table IV). These two criteria may thus be used to anticipate when geometry optimizations at the correlated level cannot be avoided. If this is the case, optimizations at the BWEN level will normally be sufficient because they lead to similar results as those at the PERTCI level (see Tables IV–V and supplementary material).

Judging from the limited data in Table IV, large semiempirical correlation effects on transition structures seem to be accompanied by similar effects in ab initio calculations. Comparing our MNDOC results in more detail with the available ab initio data[11] (also for the smaller geometry changes), we find similar qualitative trends for **6**, **8**, **14**, **15**, **17**, **22**, and **24** and partly opposite trends

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(19) The present values differ slightly from the previous ones (ref 1) due to some minor corrections (see supplementary material for details).

Table IV. Correlation Effects on Transition Structures: Selected Results

	correlation-induced geometry changes[a]					no. of important config[e]		
system	variable[b]	MNDOC BWEN	MNDOC PERTCI	6-31G* MP2[c]	c_0^2(BWEN)[d]	A	B	C
6	C^2H^4	-0.120	-0.145	-0.241	0.929	1	0	1
7	C^2H^4	-0.044	-0.054		0.922	1	0	1
	H^3H^4	-0.105	-0.111					
	$C^2C^1H^6$	-19.1	-15.8					
	$C^1C^2H^4$	-7.8	-8.3					
8	H^4H^5	-0.071	-0.059	-0.057	0.926	0	1	0
15	H^3H^4	-0.039	-0.050	-0.029	0.914	1	0	1
22	H^3H^4	-0.055	-0.075	-0.035	0.948	1	0	0
24	C^1H^5	-0.180	-0.180	-0.186	0.941	1	0	0
	$H^3O^2C^1H^4$	-10.1	-10.0	-12.6				
32	$C^1C^2O^3$	-7.9	-7.2		0.929	0	0	0
33	C^1H^4	-0.133	-0.110		0.923	0	0	0
	$C^1C^2O^3$	6.8	5.4					
	$C^1C^2H^4$	-6.1	-7.7					
35	$C^2C^1H^5$	7.7	7.5		0.886	1	2	1
36	C^2H^4	0.116	0.129		0.833	1	2	1
	O^3H^4	0.178	0.150					
	$C^1C^2O^3$	2.0	5.7					
	$C^1C^2H^4$	-9.0	-11.0					
	$C^2C^1H^5$	17.7	16.6					
37	C^1O^3	-0.052	-0.055		0.902	0	0	0
	C^1H^4	-0.107	-0.080					
38	C^1O^3	-0.108	-0.085		0.886	1	0	1
	$C^2C^1H^4$	10.2	7.2					
45	C^1H^5	-0.070	-0.081		0.905	1	0	2

[a] Differences between the SCF and correlated values for optimized bond lengths A^iB^j (in Å), bond angles $A^iB^jC^k$ (in deg), and dihedral angles $A^iB^jC^kD^l$ (in deg). The table lists all cases where the absolute difference between MNDOC SCF and PERTCI is larger than 0.05 Å for bond lengths, 5° for bond angles, and 10° for dihedral angles. [b] For numbering of atoms see Figure 1. [c] Ab initio 6-31G* data from ref 11. [d] c_0^2(BWEN) is the contribution of the closed-shell SCF determinant to the MNDOC wave function at the SCF optimized geometry. [e] A configuration Ψ_k is considered to be important if $|H_{k0}|^2(E_k - E_0)^{-1} > 0.2$ eV at the SCF optimized geometry (see text). It is assigned to class A (B, C) if all (some, none) of the MOs involved in the excitation have the same symmetry as the reaction coordinate. The reaction coordinate is totally symmetric in all cases, except for **41** (b) and **43** (b_2).

Table V. Correlation Effects on Transition Structures: Statistics[a]

		mean absolute deviations in MNDOC		
property	N[b]	SCF-BWEN	SCF-PERTCI	BWEN-PERTCI
bond lengths, Å	119	0.027	0.022	0.008
active[c]	72	0.040	0.034	0.012
passive[c]	47	0.008	0.007	0.002
bond angles, deg	70	2.9	2.8	0.8
all angles, deg	91	2.8	2.7	0.9

[a] On the basis of the optimized MNDOC geometries for all 24 transition structures studied (see supplementary material). [b] Number of comparisons. [c] "Active" bonds are broken or formed in the reaction; "passive" bonds remain formally unchanged.

for **7** and **16**. Considering the remarks in section III, a more quantitative comparison seems premature.

To summarize our discussion, we suggest some guidelines for semiempirical MNDOC studies of thermal organic reactions which are based on our present numerical results. These guidelines refer to reactions with transition states that are reasonably well described in zero order by a single SCF determinant.

(a) For given geometries, the correlation corrections to activation energies should be evaluated explicitly because they can range between 0 and more than 20 kcal/mol. BWEN can normally be used to compute these corrections, but it should be kept in mind that BWEN tends to overestimate the more reliable PERTCI or DECI values by about 20%.

(b) For the calculation of activation energies, it is justified in most cases to use SCF optimized geometries. A reoptimization at the BWEN level is recommended only for transition states with $c_0^2 < 0.90$, to avoid geometry-related errors of more than 2 kcal/mol.

(c) Correlated transition structures are normally obtained with sufficient accuracy at the BWEN level. For transition states with $c_0^2 > 0.92$ and without important excitations of class A (see above), correlated geometry optimizations seem unnecessary, in general, because the maximum correlation-induced changes are then below 0.1 Å for bond lengths and below 10° for angles.

(V) Conclusion

Correlation effects on semiempirical transition states are more important for energies than for geometries. MNDOC-BWEN calculations at SCF optimized geometries are therefore normally suitable for studying thermal organic reactions. Criteria are available when more refined treatments are necessary. Large semiempirical correlation effects on activation energies and transition structures are usually associated with qualitatively similar effects in ab initio calculations.

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Supplementary Material Available: Figures concerning the PERTCI convergence behavior with respect to *T*, tables with optimized geometries for all transition states, and some minor corrections to previous results (ref 1) (13 pages). Ordering information is given on any current masthead page.