MNDOC parameters, as long as these treatments provide a reasonable approximation to the exact MNDOC correlation energy.

The explicit inclusion of electron correlation in MNDOC does not improve the calculated heats of formation and geometries of closed-shell ground states significantly, since the correlation effects in these systems can, on the average, be taken into account by a parametrization at the SCF level. Qualitative differences between MNDOC and MNDO can thus only be expected for systems which show specific correlation effects. This will be studied in the following two papers dealing with reactive species, transition states, and excited states.

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MNDOC Study of Reactive Intermediates and Transition States

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Abstract: MNDOC calculations on reactive species are carried out for methylene, cyclobutadiene, benzyne, and [18]annulene. Transition states of "allowed" thermal reactions are studied for the 1,2 hydrogen shift in vinylidene, the disrotatory ring opening of cyclopropyl cation, and the conrotatory ring opening of cyclobutene. The MNDOC correlation effects in these examples are discussed and compared with available ab initio results. MNDOC turns out to be superior to MNDO for systems which show specific correlation effects.

Experimental evidence about reactive intermediates and transition states is difficult to obtain. Theory may therefore provide valuable information concerning the detailed course of chemical reactions, and semiempirical methods have indeed been applied successfully to the study of chemical reactions.[1]

Reactive intermediates and transition states are often characterized by unusual bonding situations where electron correlation may be expected to play an important role. In these cases, there is some ambiguity in applying current semiempirical methods such as MINDO/3[2] or MNDO[3] which have been parametrized at the SCF level; usually either an SCF or a minimal CI treatment is carried out, the choice between them being made on an empirical basis.[4] The MNDOC[5] method, on the other hand, is free from such procedural problems since it has been parametrized to completely include correlation effects, within the framework of the MNDOC model.

To establish the reliability of MNDOC for the study of chemical reactions, it would be desirable to compile some statistical analysis similar to that for closed-shell ground states.[5] Unfortunately, this is not feasible due to the lack of accurate experimental data and the computational effort involved. In the present paper, we shall instead report on the MNDOC results for seven typical examples and discuss the correlation effects involved. The performance of MNDOC will be evaluated by comparisons with MNDO results, ab initio results, and experimental data (if available).

Theoretical Approach

Unless noted otherwise, MNDOC is applied in its standard version,[5] electron correlation being treated by second-order Brillouin–Wigner perturbation theory with Epstein–Nesbet energy denominators (BWEN). For the systems studied, one complication may arise which is not encountered with closed-shell ground states: if the energy of a particular doubly excited configuration Ψ_1 is only slightly above that of the SCF configuration Ψ_0, the corresponding contribution to the perturbation energy is overestimated since the energy denominator is very small (see eq 1 in ref 5). In this case, the lowest root of a 2×2 CI involving Ψ_0 and Ψ_1 must be taken as zero-order reference state in the perturbation treatment, the perturbation summation extending over all configurations which are doubly excited with respect to Ψ_0. This procedure is denoted by BWEN1.

If the two configurations Ψ_0 and Ψ_1 are degenerate or almost degenerate, the MNDOC correlation energy will also contain significant contributions from configurations corresponding to single or double excitations from Ψ_1 (i.e., including single, double, triple, and quadruple excitations from Ψ_0). A BWEN treatment using this configuration space and a zero-order state from a 2×2 CI will be termed BWEN2.

It should be emphasized that BWEN1 and BWEN2 do not represent any "special" correlation treatments. Our general philosophy[5] is to approximate the exact MNDOC correlation energy as closely and efficiently as possible. For ground-state singlets, this is achieved by a standard BWEN treatment with one main configuration, whereas a BWEN1 or BWEN2 treatment with two main configurations is required in the cases described above. Hence, BWEN1 and BWEN2 are simply the proper versions of perturbation theory if the two lowest configurations are close in energy.

In principle, BWEN2 should always be preferred over BWEN1 since it provides a better approximation to the exact MNDOC correlation energy. In practice, however, BWEN2 is considerably slower than BWEN1 due to the larger configuration space, whereas the results are fairly similar if the two relevant configurations are not too close in energy. In the present paper, we shall therefore adopt the following convention: BWEN2 will be used if the configurations Ψ_0 and Ψ_1 are separated by less than 1 eV, and BWEN1 in all other cases where Ψ_1 is considered to be important.

In our theoretical approach, there is one more choice to be made concerning the determination of the molecular orbitals (MOs): reactive intermediates and transition states are often open-shell species which might advantageously be described by open-shell

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RHF MOs[6] such as half-electron MOs[7] rather than by standard closed-shell RHF MOs. This alternative has been examined in test calculations for three open-shell species. In each case, the MNDOC results obtained for the two sets of MOs do not differ significantly, the maximum deviations being 0.2 kcal/mol in heats of formation and 0.006 Å in optimized bond lengths. Hence, the MNDOC results do not depend critically on the MO basis used in the correlation treatment.

In the present paper, we have decided to use closed-shell RHF MOs exclusively. If, however, the need arises, e.g., if one wants to avoid symmetry-broken closed-shell SCF solutions or if the closed-shell SCF treatment does not converge, it would certainly be justified to employ half-electron open-shell RHF MOs in MNDOC.

Results for Reactive Species

In this section, we report MNDOC results for methylene **1**, square cyclobutadiene **2**, the benzyne isomers **3**–**6**, and [18]-annulene **7** (see Figure 1).

A. Methylene. The energy difference between singlet and triplet methylene has long been controversial. Recent sophisticated ab initio calculations[8–12] using correlated wave functions with large basis sets all predict a value of 10.5 ± 2.0 kcal/mol. On the basis of these calculations, the experimental value of 19.5 ± 0.7 kcal/mol from photodetachment[13] has been reinterpreted as being due to hot bands[10,11] or to the involvement of a second anion state.[10] Recent photochemical measurements establish an upper limit of 8.1 ± 0.8[14] and 9.8 ± 1.5 kcal/mol[15] for the singlet/triplet splitting. Hence, a value of about 9 kcal/mol would seem to be compatible with the present theoretical and experimental evidence.

Table I contains the MNDO, MNDOC, and experimental[14–18] results for the heats of formation and geometries of triplet and singlet methylene. Obviously, the MNDO predictions are quite inaccurate in this case, whereas the MNDOC results are in much better agreement with the experimental data. This qualitative improvement is already found at the SCF level (see Table I), indicating that it is primarily due to the MNDOC parametrization rather than to a direct correlation effect. This is easily understood from the values of the carbon resonance parameters in MNDO[3] and MNDOC[5]: the high β_s/β_p ratio in MNDO tends to favor sp hybridization and linear structures so that triplet methylene is too stable and has a bond angle which is too large. This is corrected in MNDOC by using a lower β_s/β_p ratio. Errors due to the high β_s/β_p ratio in MNDO are expected to occur only in compounds where carbon is not tetravalent (e.g., in carbenes). In these cases, MNDOC seems to be superior.

The singlet/triplet splitting of methylene has been calculated to be 24.8 kcal/mol near the Hartree–Fock limit,[19] implying an ab initio correlation effect of about 14 kcal/mol on the splitting. The corresponding MNDOC correlation effect of 4.1 kcal/mol is considerably smaller, but of the same direction.

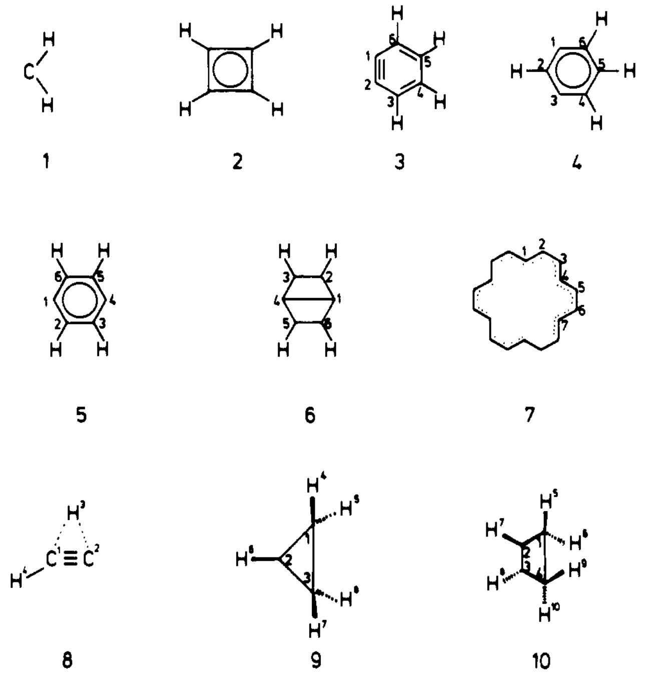

Figure 1. Reactive species and transition states studied.

Table I. MNDO and MNDOC Results[a] for Triplet ($^3B_1$) and Singlet ($^1A_1$) Methylene

		MNDO SCF	MNDOC SCF	MNDOC BWEN[b]	exptl
$^3B_1$	ΔH_f, kcal/mol	77.3	96.5	90.4	93.6[c]
	C-H, Å	1.052	1.066	1.071	1.078[d]
	HCH, deg	149.9	134.6	134.7	136[d]
$^1A_1$	ΔH_f, kcal/mol	107.4	103.8	93.6	
	C-H, Å	1.091	1.106	1.113	1.11[e]
	HCH, deg	111.1	101.5	101.6	102.4[e]
$^3B_1 \rightarrow {}^1A_1$	ΔE_{ST}, kcal/mol	30.1	7.3	3.2	~9[f]

[a] Key: heats of formation ΔH_f, bond lengths C-H, bond angles HCH, singlet/triplet splitting ΔE_{ST}. [b] BWEN1 for S_0. [c] References 14 and 16. [d] Reference 17. [e] Reference 18. [f] See text. Note that this value refers to 0 K; for comparisons at 298 K, a correction term of 1.2 kcal/mol should be subtracted.[14]

B. Square Cyclobutadiene. For unsubstituted cyclobutadiene, it has long been unclear whether the ground state is a singlet or a triplet, with a rectangular or square geometry. Recent IR studies on matrix-isolated molecules[20–22] no longer support a square geometry and have been interpreted in terms of a rectangular singlet ground state.[22] This is in agreement with all recent theoretical studies[23–25] and also with the MNDO and MNDOC results.

In the present context, square cyclobutadiene is of particular interest. Table II gives the singlet/triplet splitting for square cyclobutadiene as obtained from MNDOC and ab initio calculations; no experimental information is available.

At the SCF level, the square singlet and triplet are degenerate in MNDOC: the two singly occupied π MOs are localized at the 1,3- and 2,4-positions of the ring, respectively, so that their exchange integral K_{12} and the singlet/triplet splitting $2K_{12}$ vanish in MNDOC approximation. Note that this degeneracy is inherent to the integral approximation used, and completely independent

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Table II. Singlet/Triplet Splitting ΔE_{ST} for Square Cyclobutadiene

method	ΔE_{ST}, kcal/mol[a]	ref
MNDOC, SCF	0.0	
MNDOC, π-BWEN[b]	9.8	
MNDOC, BWEN[b]	9.4	
6-31G*, SCF	−6.9	25
6-31G*, π-CI[c]	8.2	25
6-31G*, CI[c]	11.0	25
DZP-basis, SCF[d]	−6.4	23
DZP-basis, PERT[d]	7.3	23

[a] For positive values, the singlet is more stable. [b] BWEN2 for the singlet. π-BWEN involves π MOs only. [c] CI with selection of configurations. π-CI involves π MOs only. [d] Double ζ-plus-polarization (DZP) basis, special perturbation treatment of correlation.

of the actual values of the MNDOC parameters. Hence, the greater stability of the square singlet cyclobutadiene in MNDOC is a pure correlation effect.

The MNDOC results are in qualitative agreement with the ab initio ones[23-26] (see Table II). The ab initio calculations predict the triplet to be slightly more stable than the singlet at the SCF level, but correlation effects favor the singlet somewhat more than in MNDOC. Consequently, the singlet/triplet splittings from MNDOC and from ab initio calculations are quite similar.

Finally, both MNDOC and the ab initio studies agree in that the stabilization of the square singlet cyclobutadiene is mostly due to a specific correlation effect among the π electrons (see Table II) which has been termed "dynamic spin polarization".[23]

C. Benzyne Isomers. Experimentally, *o*-benzyne has been studied by matrix-isolation spectroscopy.[27,28] *m*-Benzyne,[29,30] *p*-benzyne,[31] and butalene[32] have been invoked as intermediates in organic reactions. *p*-Benzyne behaves like a biradical[31] whereas *m*-benzyne may possibly be described by a closed-shell bicyclo[3.1.0]hexatriene structure.[29,30].

Theoretically, the benzyne isomers have been investigated by MINDO/3[33] and by the ab initio GVB method by using a 4-31G basis set.[34] Although each of the isomers is interesting in its own right, their theoretical study also allows comparisons concerning the relative stability of isomeric closed-shell and biradicaloid species.

Table III lists the MNDOC optimized geometries, at the SCF, 2 × 2 CI, and BWEN1 levels. For *o*-benzyne **3** and butalene **6**, the SCF and 2 × 2 CI structures are almost identical, whereas large changes are encountered for *p*-benzyne, and especially for *m*-benzyne. In the latter case, the SCF geometry corresponds to a closed-shell bicyclic compound, and the 2 × 2 CI geometry to a biradicaloid species, in agreement with previous results;[34] both structures are the only minima on the respective potential surfaces.[35] These findings illustrate that the eigenvector of a minimal CI treatment is required for a zero-order description of biradicaloid systems; this, of course, is the usual practice in semiempirical calculations.[4] Comparing the 2 × 2 CI and BWEN1 geometries, only small changes are found which are within the normal range.[5]

Table III. MNDOC Geometries of Benzyne Isomers[a]

isomer[a]	variable[b]	SCF	2 × 2 CI	BWEN1[c]
3	C^1–C^2	1.243	1.243	1.281
	C^2–C^3	1.381	1.381	1.388
	C^3–C^4	1.409	1.409	1.418
	C^4–C^5	1.425	1.425	1.452
4	C^1–C^2	1.372	1.377	1.379
	C^1–C^3	1.582	2.204	2.186
	C^3–C^4	1.379	1.377	1.382
	C^4–C^5	1.420	1.406	1.415
5	C^1–C^2	1.344	1.370	1.363
	C^2–C^3	1.466	1.420	1.453
	C^1–C^4	2.604	2.624	2.653
6	C^1–C^2	1.388	1.389	1.397
	C^2–C^3	1.442	1.444	1.453
	C^1–C^4	1.604	1.599	1.613

[a] The numbering refers to Figure 1. Symmetry restrictions: C_{2v} for 3 and 4, D_{2h} for 5 and 6. [b] Bond lengths A–B in Å. [c] The BWEN results for 3 and 6 are almost identical with the BWEN1 ones.

Table IV. Relative Energies (kcal/mol) of the Benzyne Isomers[a]

method	3	4	5	6
MINDO/3, 2 × 2 CI[33]	0.0	−7.1	2.6	38.5
MNDO, 2 × 2 CI	0.0	−6.9	−3.5	26.2
MNDOC, 2 × 2 CI	0.0	−10.4	−1.3	31.3
MNDOC, BWEN1	0.0	7.4	17.9	41.7
4-31G, GVB[34]	0.0	14.5	23.3	77.2[b]

[a] At optimized geometries (partial optimization for GVB). [b] This value "might be too large by as much as a factor of 2".[34]

Table IV shows the relative energies of the benzyne isomers as obtained by various methods. At the 2 × 2 CI level, the semiempirical MINDO/3, MNDO, and MNDOC methods all give qualitative similar results, the meta isomer being the most stable one. Inclusion of electron correlation in MNDOC at the BWEN1 level preferentially stabilizes the ortho isomer which is now lowest in energy, in agreement with the GVB calculations. The difference between the MNDOC correlation energies of the various isomers are of the order of 15 kcal/mol.

These results suggest that a minimal CI treatment might overestimate the stability of biradicaloid species although their geometries can be reproduced reasonably. Any such bias in favor of biradicaloids should, however, be smaller in saturated than in unsaturated systems since the MNDOC correlation effects are generally smaller in saturated systems.[5]

In spite of quantitative discrepancies, the present results confirm the major conclusion from the MINDO/3 study[33] that *o*-benzyne and *m*-benzyne are of comparable stability. With regard to *m*-benzyne, our calculations support a biradicaloid structure[34] rather than a closed-shell bicyclic structure.[29,30]

D. [18]Annulene. Both "aromatic" and "nonaromatic" geometries have been suggested for [18]annulene, an "aromatic" geometry being characterized by D_{6h} symmetry and almost equal CC bond lengths, and a "nonaromatic" one by D_3 or D_{3h} symmetry and strong bond alternation.

Experimentally, the gas-phase structure of [18]annulene is not known. The X-ray analysis of the solid has been interpreted in terms of a D_{6h} geometry with "aromatic" CC bond lengths.[36] The UV spectrum in solution[37] does not allow unambiguous structural conclusions.[38,39]

"Nonaromatic" geometries have been obtained by molecular mechanics[39] (D_3 symmetry) and MINDO/3[40] (D_{3h} symmetry). This deviation from the X-ray structure has been rationalized by possible differences between the crystal and gas-phase structures[39] and by possible complications in the analysis of the X-ray data.[40]

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Table V. MNDOC SCF Structures for [18]Annulene[a]

variable[b]	D_{3h}	D_{6h}	exptl[c]
C^1-C^2	1.346	1.397	1.382
C^2-C^3	1.467	1.402	1.419
C^3-C^4	1.346	1.397	1.382
C^4-C^5	1.459	1.397	1.382
C^5-C^6	1.351	1.402	1.419
$C^1C^2C^3$	124.8	125.3	123.8
$C^2C^3C^4$	130.5	130.7	127.5
$C^3C^4C^5$	125.6	125.3	123.8
C^3-H	1.094	1.095	
C^4-H	1.095	1.095	
C^5-H	1.095	1.095	
HC^3C^2	114.4	116.2	
HC^4C^5	113.0	114.7	
HC^6C^7	118.0	116.2	

[a] The numbering refers to Figure 1. Some of the data given are redundant due to symmetry (D_{6h}). [b] Bond lengths A–B in Å, bond angles ABC in degree. [c] Reference 36.

Table VI. [18]Annulene: Energy of D_{6h} Relative to D_{3h} Species[a]

method	ΔE, kcal/mol	method	ΔE, kcal/mol
MINDO/3, SCF[b]	25.7	MNDOC, π-BWEN[c]	7.7
MNDO, SCF	27.2	MNDOC, BWEN	7.6
MNDOC, SCF	27.0	MNDOC, final[d]	−1.1

[a] MNDO and MNDOC results at MNDOC SCF optimized geometries. [b] Reference 40. [c] π-BWEN involves π MOs only. [d] Including the Davidson correction (see text).

According to recent CNDO-type calculations,[41] electron correlation reverses the relative stabilities of the "aromatic" and "nonaromatic" forms. The origin of this correlation effect has previously been traced to the singlet instability of the closed-shell SCF solution for the higher annulenes.[61] Correspondingly, an unrestricted[62] MNDO treatment of [18]annulene[63] favors the "aromatic" over the "nonaromatic" form.

Table V lists the MNDOC SCF optimized geometries for the D_{3h} and D_{6h} species. Relative energies at these SCF geometries[42] are given in Table VI. At the restricted SCF level, all semiempirical MO methods applied predict the D_{3h} structure to be more stable than the D_{6h} one by more than 20 kcal/mol. However, the MNDOC calculations confirm[41] that electron correlation preferentially stabilizes the D_{6h} species. Correlation among the π electrons favors the D_{6h} structure by 19.3 kcal/mol, in good agreement with a previous PPP calculation.[41] However, σ correlation has essentially no effect (see Table VI), so that the D_{3h} form is still more stable at the MNDOC BWEN level, in contrast to previous results.[41,43]

In molecules of the size of [18]annulene, higher excitations already contribute significantly to the correlation energy.[44] If the influence of these higher excitations is included via the Davidson correction,[44,45] the D_{6h} species is further favored and becomes the most stable structure. Although the final MNDOC energy difference of 1.1 kcal/mol is too small to be conclusive, it is obvious that electron correlation is very important in the [18]annulene system. If the gas-phase structure is indeed "aromatic", this may be regarded as a correlation effect.

Finally, we note that the gas-phase photoelectron spectrum of [18]annulene might allow structural deductions. In Koopmans' approximation,[46] MNDOC predicts the first ionization potential to be 7.10 (D_{6h}) or 8.26 eV (D_{3h}); the MNDO values are 6.96 and 8.15 eV, respectively. Since the first π-ionization potential normally is quite unaffected by electron correlation, an "aromatic" structure is probable if the first photoelectron band lies at or below 7 eV, and a "nonaromatic" one if it is at or above 8 eV.

Table VII. Transition-State Structures

TS[a]	variable[b]	MINDO/3 SCF	MNDO SCF	MNDOC SCF	MNDOC BWEN	ab initio[c]
8	C^1C^2		1.270	1.261	1.287	1.247
	C^1H^3		1.371	1.402	1.386	1.423
	C^2H^3		1.322	1.269	1.297	1.220
	C^1H^4		1.059	1.067	1.071	1.056
	$H^4C^1C^2$		167.0	172.7	171.1	177.8
9	C^1C^2	1.378	1.430	1.420	1.454	
	C^1C^3	1.839	1.757	1.732	1.623	
	$H^4C^1C^2$	120.0	119.0	118.8	118.2	
	$H^5C^1C^2$	130.0	126.5	126.2	124.1	
	H^6-$C^1C^2C^3$	29.3	20.9	25.2	19.3	
	$H^4H^5C^1$-$C^1C^2C^3$	56.8	67.6	67.2	75.9	
10	C^1C^2	1.388	1.417	1.403	1.421	1.446
	C^2C^3	1.418	1.406	1.402	1.401	1.400
	C^1C^4	2.058	2.117	2.098	2.142	2.266
	$C^1C^2C^3$	102.0	103.1	103.0	104.0	
	$C^4C^1C^2$	75.8	74.5	74.7	74.2	
	$C^1C^2C^3C^4$	21.0	22.6	22.1	19.4	23.0
	$C^1C^2C^3$-$C^1H^5H^6$	49.2	50.8	49.9	52.4	48.5

[a] See Figure 1 for the numbering of the transition states and for the geometry definitions. [b] Bond lengths AB in Å, bond angles ABC, dihedral angles ABCD, angles A–BCD of A–B with the plane BCD, angles ABC–DEF between the planes ABC and DEF, all angles in degree. [c] For **8**, 4-31G SCF structure; for further comparisons see ref 51. For **10**, partially optimized structure using an essentially minimal basis and limited CI; see ref 58.

Results for Transition States

In this section, we shall examine the following three simple hydrocarbon reactions: (A) the 1,2 hydrogen shift in vinylidene to yield acetylene, (B) the disrotatory ring opening of cyclopropyl to allyl cation, and (C) the conrotatory ring opening of cyclobutene to butadiene. Since all these reactions are "allowed", the SCF configuration provides the appropriate zero-order description for the transition states, and electron correlation can be treated by the standard BWEN procedure. The 2 × 2 CI results will therefore not be given; they differ from the SCF results only slightly.

The transition states for the three reactions (**8**–**10**, see Figure 1) are located by minimizing the norm of the gradient.[47] The resulting structures are listed in Table VII (including only the essential variables for **9** and **10**), and the activation energies are given in Table VIII. Along with the MNDOC results, MINDO/3, MNDO, and ab initio data are included to allow comparisons to be made in the following discussion.

A. The 1,2 Hydrogen Shift in Vinylidene. 1,2 hydrogen shifts are a common rearrangement for reactive species, e.g., for carbenes, nitrenes, and vinylidenes.[48] The parent vinylidene molecule seems to be an intermediate in the reaction of C_2 with hydrogen-containing compounds to yield acetylene.[48,49] The activation energy for the hydrogen shift has not been measured, but it must be very small considering the short lifetime of vinylidene.

On the theoretical side, there are two recent ab initio studies of this reaction using double-ζ (DZ) as well as double-ζ-plus-polarization (DZP) basis sets and treating electron correlation explicitly.[50,51] Both studies arrive at essentially the same results

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(42) The use of SCF geometries in BWEN studies has previously been justified for MNDOC.[5]

(43) There is no obvious reason for this discrepancy. Note, however, that the present study includes all doubly excited configurations (ca. 580.000), whereas the former one[41] selects only a small fraction (ca. 5.000).

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(45) Cf. eq 3 in ref 5, using E^{BWEN} and $C^{\mathrm{BWEN}}{}_0$ instead of E^{DECl} and $C^{\mathrm{DECl}}{}_0$.

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Table VIII. Activation Energies (kcal/mol) for Reactions A, B, and C[a]

method	A	B	C
MINDO/3, SCF		2.3	49.0
MNDO, SCF	30.2	4.6	49.9
MNDOC, SCF	24.0	4.5	57.8
MNDOC, BWEN[b]	19.0		50.1
MNDOC, BWEN	19.2	0.8	50.0
ab initio, SCF	26.1[c]	1.6[g]	68.1[j]
ab initio, CORR	18.5[d]	1.3[h]	48.8[k]
ab initio, SCF	16.4[e]	4/0[i]	83/45[l]
ab initio, CORR	8.1[f]		

[a] The reactions are defined in the text. Unless noted otherwise, all values refer to geometries optimized for the method given. [b] MNDOC BWEN values at MNDOC SCF geometries. [c] 4-31G basis.[51] [d] 4-31G basis, correlation by coupled cluster theory, at SCF geometries.[51] [e] 6-31G* basis.[51] [f] 6-31G* basis, correlation by fourth-order Mφller-Plesset theory, at SCF geometries.[51] [g] Double-ζ basis.[53] [h] Double-ζ basis, limited CI.[53] [i] STO-3G/4-31G at STO-3G geometries.[52] [j] Essentially minimal basis.[58] [k] Essentially minimal basis, limited CI.[58] [l] STO-3G/4-31G at PRDDO geometries.[54]

so that only one set of data[51] is included in Tables VII and VIII.

The optimized MNDOC SCF and DZ SCF geometries for the transition state are fairly similar (see Table VII). Likewise, inclusion of electron correlation in MNDOC BWEN does not change the transition-state structure significantly; the deviations from the SCF values are slightly larger than for closed-shell ground states[5] but still of the same order of magnitude. This may be taken as a justification for using SCF optimized transition-state geometries in correlation studies, as is done in the ab initio investigations.[50,51]

The MNDOC SCF and DZ SCF activation energies again agree very well (see Table VIII). In both cases, the activation energy is reduced to a value of ca. 19 kcal/mol by including electron correlation, the correlation effect being somewhat larger in the ab initio case (7.6 kcal/mol) than in MNDOC (4.8 kcal/mol). Judging from the experimental evidence,[48,49] this value for the activation energy is still too high. A correlated DZP calculation is required (see Table VIII) in order to obtain a more realistic prediction.

B. The Disrotatory Ring Opening of Cyclopropyl Cation. Experimentally, it is not known whether the cyclopropyl cation exists as a local minimum on the potential surface. According to recent calculations[52-54] and our present results, the energy of the cyclopropyl cation relative to the allyl cation lies in the range 28–49 kcal/mol (e.g., MNDO 36.9, MNDOC SCF 33.9, MNDOC BWEN 35.9, STO-3G[52] 27.8, 4-31G[52] 46.5, 6-31G*[52] 39.2). All treatments[52-55] predict little or no activation energy (0–8 kcal/mol) for the disrotatory ring opening (see Table VIII).

This reaction can therefore be taken as an example to study correlation effects on reactions with small barriers. Inspection of Table VII shows that the transition-state structure is significantly changed by correlation effects, the length of the breaking CC bond being reduced by 0.109 Å. The SCF optimized geometry of the transition state cannot be taken as a reasonable approximation to the BWEN one; doing so, one obtains a negative activation energy at the BWEN level. Hence, geometries should be optimized with inclusion of electron correlation if reactions with small barriers are studied.

In MNDOC, correlation effects reduce the activation energy for the disrotatory ring opening by 3.7 kcal/mol (see Table VIII). This is a larger change than in a previous ab initio study[53] which, however, employed only partial geometry optimization. The reduction of the activation energy by electron correlation casts further doubt[52] on the existence of the cyclopropyl cation.

C. The Conrotatory Ring Opening of Cyclobutene. As a classical example of an electrocyclic reaction, the ring opening of cyclobutene has been thoroughly studied both experimentally[56,57] and theoretically.[47,54,58,59] The reaction follows a stereospecific conrotatory mode,[60] the experimental activation energy being 32.9 ± 0.7 kcal/mol.[57]

With regard to the transition-state structure (see Table VII), the results are analogous to those for reaction A (see above): the optimized MNDOC and ab initio geometries are qualitatively similar. Inclusion of electron correlation in MNDOC produces only small structural changes, the largest deviation being found for the breaking CC bond which is lengthened by 0.044 Å due to correlation. Therefore, MNDOC BWEN calculations using SCF optimized and BWEN optimized geometries yield almost identical activation energies (discrepancy of 0.1 kcal/mol).

All theoretical treatments applied predict activation energies for the ring opening which are too high (see Table VIII). In the case of the semiempirical methods, this is partly due to overestimating the stability of cyclobutene.[2,3,5] The calculated activation energies for the reverse reaction, the ring closure of *trans*-butadiene, are in better agreement with experiment (e.g., MNDOC SCF 53.3, MNDOC BWEN 46.2, exptl 44.4 kcal/mol).

In MNDOC, the activation energy for the ring opening is reduced by 7.8 kcal/mol upon inclusion of electron correlation. The correlation effect in MNDOC is thus considerably smaller than in an ab initio calculation (19.3 kcal/mol)[58] but of the same direction.

Discussion

For closed-shell ground states, the MNDOC and MNDO results turn out to be very similar[5] since there are only "average" correlation effects in these systems. The preceding sections show that MNDOC and MNDO may strongly differ in their predictions for systems with specific correlation effects.

For the reactive species studied, these differences are of the order of 10–30 kcal/mol. Judging from available experimental and ab initio data, the MNDOC results are superior in these cases. There are two possible reasons for the discrepancies between MNDOC and MNDO. First, a comparison of results at the SCF level reveals the effects of using different parameter sets;[3,5] any improvement with MNDOC at this level (e.g., for methylene) is an "indirect" consequence of electron correlation due to its inclusion in the MNDOC parametrization. Second, any change of MNDOC predictions in going from the SCF to the BWEN level can be regarded as a "direct" correlation effect (cf. cyclobutadiene, benzyne, [18]annulene) which is largely independent of the actual values of the parameters. Note in this connection that BWEN test calculations with MNDO parameters normally yield correlation energies which are similar to the MNDOC ones; however, such MNDO BWEN calculations are, of course, inconsistent since MNDO has been parametrized at the SCF level.[3]

For the three chemical reactions investigated, inclusion of electron correlation in MNDOC always lowers the activation energy, typically by about 5 kcal/mol. For reactions A and C where experimental evidence is available, this lowering improves the calculated values although it corrects for only part of the error at the SCF level.

If one may generalize from the three examples studied, the

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MNDOC correlation effects on the activation energy of "allowed" chemical reactions are rather small, while the SCF optimized and BWEN optimized transition-state structures are quite similar (except for reactions with small barriers). This is rationalized by the fact that the BWEN wave functions of these "allowed" transition states are strongly dominated by the SCF configuration Ψ_0; the corresponding coefficients C^{BWEN}_0 are almost as high as in the case of the reactants and products. These findings may offer an explanation for the success of previous uncorrelated semiempirical studies,[1] at least for "allowed" reactions.

When comparing the MNDOC and ab initio results, it is gratifying that the predicted correlation effects on relative energies are always of the same direction, usually being somewhat larger in the ab initio case (typically by a factor of 2). In some systems (cf. methylene, cyclobutadiene), the final MNDOC and ab initio results are rather close since the discrepancies at the SCF level are diminished by the correlation corrections.

With regard to applications of MNDOC, it should be noted that the correlation effects encountered are often due to a small number of specific interactions, e.g., the interactions between the π electrons in cyclobutadiene and [18]annulene (cf. Tables II, VI). In these cases, it is feasible to truncate the MO basis for the correlation treatment if one is interested in relative energies only. The calculated heats of formation will then lose any absolute meaning since part of the MNDOC correlation energy is neglected, but relative energies may still be reproduced reliably. From a practical point of view, an even more important simplification seems to be justified in the MNDOC study of ground-state potential surfaces: judging from the examples investigated, electron correlation influences relative energies appreciably, whereas optimized geometries are affected only slightly (see reaction B for an exception). Therefore, to a good approximation, geometry optimizations at the BWEN level can normally be avoided in the MNDOC study of thermal reactions. The structures of the species involved may instead be optimized at the zero-order level (SCF or minimal CI) while the relative energies are calculated with inclusion of electron correlation. This approach is computationally feasible and should normally be sufficient to reveal any particular correlation effect in chemical reactions.

Conclusions

The present study shows MNDOC to be complementary to MNDO. Both methods are of similar accuracy for closed-shell ground states,[5] but MNDOC turns out to be superior for systems with specific correlation effects. Hence, while a simple MNDO calculation is adequate for closed-shell molecules, MNDOC can also be applied in cases where an uncorrelated semiempirical treatment is inappropriate. This extended range of application represents the main improvement of MNDOC over previous semiempirical treatments.

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MNDOC Study of Excited States

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Abstract: MNDOC calculations of excited states are carried out by using a CI perturbation treatment of electron correlation. MNDOC results for vertical and adiabatic excitation energies, geometries, and dipole moments are reported and compared with experimental and ab initio data. On the basis of this evidence, the application of MNDOC to the study of photochemical reactions is discussed.

Excited states are more difficult to describe theoretically than ground states because electron correlation plays a more important role. Whereas the molecular ground state is usually well represented by the closed-shell SCF configuration, there are normally several configurations which are close in energy and interact strongly to produce a particular excited state.

Consequently, electron correlaction is included explicitly in semiempirical treatments which have been designed for the calculation of vertical excitation energies,[1] most notably PPP,[2,3] CNDO/S[4] and its variants,[1,5] INDO/S,[1,6] and LNDO/S;[7] among these methods, only LNDO/S includes doubly or more highly excited configurations and employs large configuration spaces. However, none of these methods seems to be particularly suited to the study of excited-state surfaces[8] since none has been parametrized to reproduce geometries or relative stabilities of different molecules; hence there are only few applications of this kind.[8,9] On the other hand, semiempirical treatments such as MINDO/3[10] and MNDO,[11] which are successful for ground-state surfaces, may encounter problems with excited states[7] since they have been parametrized at the SCF level. These methods have therefore rarely been applied to excited states[12] and their reactions;[13,14]

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