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.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (through a Liebigstipendium). The calculations were carried out on the TR 440 computer of the Universität Marburg and the IBM 370-168 computer of the Technische Hochschule Darmstadt.

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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(2) Parr, R. G. "The Quantum Theory of Molecular Electronic Structure"; W. A. Benjamin: New York, 1963.

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(8) Michl, J., In "Modern Theoretical Chemistry. Semiempirical Methods of Electronic Structure Calculation"; Segal, G. A., Ed.; Plenum Press: New York, 1977; Vol. 8, Chapter 3.

(9) van der Lugt, W. Th. A. M.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 6042.

(10) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.

(11) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(12) Dewar, M. J. S.; Olivella, S. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 829.

(13) Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1974**, *96*, 7578, and following papers.

(14) Dewar, M. J. S.; Doubleday, C. *J. Am. Chem. Soc.* **1978**, *100*, 4935.

0002-7863/81/1503-1425$01.25/0

usually only the lowest singlet and triplet excited states have been studied with the assumption that they can be described by a single configuration[12,13] or by a limited configuration interaction (CI).[14]

In this situation, it is obviously desirable to test the performance of the MNDOC method for excited-state surfaces. MNDOC would seem to be promising since it gives reasonable results for ground-state surfaces[15,16] (like MINDO/3, MNDO) and since it includes electron correlation explicitly (like LNDO/S). The present paper reports MNDOC results for vertical and adiabatic excitation energies, for geometries, and for charge distributions in excited states.

Theoretical Approach

According to our general philosophy,[7,15] the exact MNDOC correlation energy for any given state should be approximated as closely and efficiently as possible. For ground states, a simple perturbation treatment (BWEN[15] with the variants BWEN1, BWEN2[16]) is adequate for this purpose, whereas a CI perturbation treatment[17] is required in the case of excited states. Since the latter treatment has previously been described in detail,[17] we shall only review some essential points.

First suppose that a particular excited state can be characterized by one main configuration (MC) Ψ_i. For a reasonably complete treatment of correlation, the configuration space will include all spin and symmetry adapted configurations which are singly or doubly excited with respect to Ψ_i. This involves at most triple excitations from the closed-shell SCF configuration Ψ_0 if Ψ_i is singly excited with respect to Ψ_0. A configuration Ψ_k from this space is selected to belong to the set of strongly coupled configurations if its interaction $|\mathbf{H}_{ki}|^2(E_k - E_i)^{-1}$ with the main configuration Ψ_i exceeds a threshold value T (matrix element $\mathbf{H}_{ki}$, Hartree–Fock configuration energies E_k and E_i).[18] After the selection procedure, the CI matrix for the selected configurations is calculated and diagonalized, which yields the SELCI energy of the excited state. The PERTCI energy is obtained by adding the contributions from the remaining configurations as evaluated by second-order BWEN perturbation theory.

If an excited state is characterized by more than one main configuration,[19] the configuration space contains single and double excitations from all main configurations; this may, e.g., involve quadruple excitations from the closed-shell SCF configuration. In this case, the selection procedure makes use of selection vectors[17] obtained by diagonalizing the CI matrix of the main configurations. With regard to all other aspects, the CI perturbation treatment is carried out as described before.

The threshold parameter T determines the partitioning of the configuration space. The limit $T = 0$ corresponds to a pure CI treatment, and the limit $T = \infty$ to a pure BWEN perturbation treatment using the main configuration (or the selection vector[17]) as the zero-order function. In previous semiempirical calculations (LNDO/S),[7] values around $T = 0.007$ eV have been chosen because the corresponding PERTCI results are very close to the pure CI results. With MNDOC, even larger values of the threshold parameter have been tested, and it turns out that the MNDOC PERTCI excitation energies for $T = 0.1$ eV are only slightly different from those for $T = 0.007$ eV, the average absolute deviation for all excitations studied (see results) being 0.04 eV, with a maximum of 0.14 eV. This demonstrates one of the strengths of the PERTCI method, that the results are rather insensitive to the actual value of T chosen.[17] When going from $T = 0.007$ eV to $T = 0.1$ eV, the number of selected configurations[20] is typically reduced by a factor of 10, which significantly improves the computational efficiency without impairing the accuracy. Hence the threshold criterion $T = 0.1$ eV will be used as a standard in MNDOC calculations for excited states.

This choice of threshold parameter in MNDOC leads to the selection of typically 2–15 configurations from a space of several hundred or thousand. Our approch is thus essentially perturbational using a very small CI vector as zero-order function. This CI vector is composed of those few configurations which interact too strongly to be properly described by perturbation theory.

For excited states, the term "MNDOC results" will thus refer to a MNDOC PERTCI treatment (closed-shell RHF MOs, 1 MC, $T = 0.1$ eV). This treatment is expected to provide a reasonable approximation to the exact MNDOC correlation energy. If this is not true for a particular excited state, systematic improvements are possible by lowering the threshold parameter and by increasing the number of main configurations; these calculations will accordingly be specified in the following section. Thus the CI perturbation treatment will always allow for a systematic approach[7,17] to the exact MNDOC correction energy.

Results

In this section, we report MNDOC energies, geometries, and charge distributions in excited states. Since MNDOC makes use of a valence basis set of atomic orbitals, Rydberg states[21,22] cannot be treated properly. Therefore we shall only deal with valence excited states, particularly those for which experimental data[21,22] or recent ab initio calculations are available.

Table I lists vertical excitation energies of 12 simple molecules. MNDOC energies of the main configurations (virtual orbital approximation, VO) are given along with the SELCI and PERTCI results. For the sake of comparison, MNDO PERTCI excitation energies are also included since this will clarify the influence of the parametrization on the results. The values in Table I are differences between the energies of the respective excited state and the ground state at the experimental ground-state geometry. The ground state is treated at the same level of approximation as the excited state (i.e., SCF, SELCI, PERTCI); using PERTCI rather than the usual[15] BWEN energies for the ground states does not affect our final results significantly since the two energy values are always very similar.[23]

Inspection of Table I shows that the MNDOC vertical excitation energies (PERTCI) are uniformly too low, the average absolute error being 0.94 eV for the 35 excitations studied.[24] Hence MNDOC is not competitive with semiempirical methods specifically designed for spectroscopic studies; the recent LNDO/S[7] treatment, e.g., yields errors of the order of 0.2 eV for hydrocarbons. MNDOC is, however, clearly superior to MNDO which predicts extremely low excitation energies, with an absolute average error of 1.38 eV (PERTCI, cf. Table I). The improvement of MNDOC over MNDO must be due to the different parametrization since this constitutes the only difference between the two sets of calculations. In particular, the higher resonance parameter for the carbon 2p electrons in MNDOC[11,15] will lead to higher excitation energies compared to MNDO, e.g., for π–π^* transitions. Judging from the remaining errors in MNDOC, however, still higher resonance parameters would be required for better agreement with experiment.

Usually the sequence of the excited states is correctly given by MNDOC, being again superior to MNDO (cf. cyclopropene in Table I). More significantly, the spacings between various excited

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[15] Thiel, W. *J. Am. Chem. Soc.* **1981**, *103*, first of three papers in this issue.

[16] Thiel, W. *J. Am. Chem. Soc.* **1981**, *103*, second of three papers in this issue.

[17] Hase, H. L.; Lauer, G.; Schulte, K.-W.; Schweig, A. *Theor. Chim. Acta* **1978**, *48*, 47.

[18] In addition, the (less important) energy gap criterion[7,17] is used for the selection.

[19] This may be decided, e.g., by symmetry arguments or by inspection of the PERTCI wave function for 1 MC.

[20] Typical example: ^1A_u state of *trans*-glyoxal, 1793 configurations. Selected: 74 for $T = 0.007$ eV, 5 for $T = 0.1$ eV (MNDOC).

[21] Herzberg, G. "Molecular Spectra and Molecular Structure. Electronic Spectra and Electronic Structure of Polyatomic Molecules"; Van Nostrand: Princeton, 1966; Vol. 3.

[22] Robin, M. B. "Higher Excited States of Polyatomic Molecules"; Academic Press: New York, 1974.

[23] For saturated ground states, the results are often identical since no excited configuration is selected with $T = 0.1$ eV. For unsaturated ground states, the SELCI space usually contains 2–5 configurations.

[24] Note that the experimental values are sometimes not very precise due to broad bands.

Table I. Vertical Excitation Energies (eV)

molecule	state[a]	MNDO[b] PERTCI	MNDOC VO	MNDOC[b] SELCI	MNDOC[b] PERTCI	exptl	ref
C_2H_4	$^3B_{1u}$	2.53	2.92	3.25	3.22	4.4	*c*
	$^1B_{1u}$	5.99	6.51	6.71	6.64	7.65	*d*
C_2H_2	$^3\Sigma_u^+$	3.41	4.59	4.52	4.37	5.2	*e*
	$^3\Delta_u$	4.44	5.25	5.40	5.36	6.0	*e*
	$^1\Sigma_u^-$	5.30	5.83	6.14	6.20		
	$^1\Delta_u$	5.74	7.80	6.62	6.65	7.4	*e*
$CH_2{=}CHCH_3$	$^3A'$	2.48	3.07	3.22	3.14		
	$^1A'$	5.72	6.30	6.30	6.31	7.19	*f*
trans-2-butene	^3B_u	2.35	2.99	2.92	2.98	4.2	*g*
	^1B_u	5.44	6.01	6.25	5.97	7.08	*f*
1,3-butadiene	^3B_u	2.03	2.95	2.57	2.53	3.2	*h*
	^3A_g	3.06	4.80	3.66	3.81	4.95	*h*
	^1A_g	4.25	6.63	4.85	5.17	5.80	*h*
	^1B_u	4.94	5.33	5.61	5.38	5.92	*h*
cyclopropene	$^3B_2$	2.53	3.17	3.19	3.23	4.16	*i*
	$^1A_2$	5.51	6.03	5.71	5.45	6.45	*j*
	$^1B_2$	5.18	6.00	5.86	5.77	7.19	*j*
	$^1A_1$	6.87	7.69	7.29	6.82	8.06	*j*
benzene	$^3B_{1u}$	2.13	3.44	2.80	2.82	3.89	*k*
	$^3E_{1u}$	2.88	3.44/3.97	3.58	3.50	4.85	*k*
	$^3B_{2u}$	4.07	3.97	4.75	4.62	5.69	*k*
	$^1B_{2u}$	2.78	5.41	3.34	3.45	4.89	*k*
	$^1B_{1u}$	4.29	5.58	4.78	4.81	6.2	*k*
	$^1E_{1u}$	5.24	5.41/5.58	6.01	5.82	6.95	*k*
pyridine	$^1B_1$	4.05	5.00	4.35	4.10	4.51	*d*
	$^1B_2$	3.61	5.24	4.05	4.08	5.00	*e*
	$^1A_1$	4.75	5.57	5.13	5.26	6.45	*e*
	$^1B_2$	5.42	5.98	6.15	5.84	7.23	*e*
	$^1A_1$	5.88	6.17	6.60	6.42	7.23	*e*
CH_2O	$^3A_2$	2.75	2.73	2.92	2.74	3.3	*l*
	$^1A_2$	2.94	3.16	3.11	2.97	4.2	*l*
	$^3A_1$	5.16	4.73	5.03	5.10	5.6-6.2	*l*
CH_2CO	$^3A_2$	1.66	2.09	2.05	1.91		*m*
	$^1A_2$	1.68	2.35	2.08	1.96	3.84	*m*
	$^3A_1$	2.18	2.48	2.92	2.67		*m*
HCCCHO	$^3A''$	2.98	3.67	2.92	2.88	2.99	*n*
	$^1A''$	3.23	4.03	3.29	3.17	3.56	*o*
$(CHO)_2$	^3A_u	2.18	2.78	2.31	2.20	2.38	*d*
	^1A_u	2.40	3.11	2.65	2.47	2.73	*d*

[a] The states correspond to π-π^* excitations, with the following exceptions: σ-π^* for $^1A_2$ in cyclopropene; σ-σ^* for $^1A_1$ in cyclopropene; n-π^* for $^1B_1$ in pyridine, $^3A_2$ and $^1A_2$ in formaldehyde, $^3A''$ and $^1A''$ in propynal, ^3A_u and ^1A_u in *trans*-glyoxal.

[b] Standard SELCI and PERTCI except 2 MC for acetylene and benzene (all states), for ^1A_g in *trans*-butadiene, and for $^1B_2$ in pyridine.

[c] Doering, J. P.; Williams, A. J. *J. Chem. Phys.* 1967, *47*, 4180.

[d] Reference 21.

[e] Dance, D. F.; Walker, I. C. *Chem. Phys. Lett.* 1973, *18*, 601.

[f] Reference 22.

[g] Moore, J. H., Jr. *J. Phys. Chem.* 1972, *76*, 1130.

[h] Reference 33.

[i] Sauers, I.; Grezzo, L. A.; Staley, S. W.; Moore, J. H., Jr. *J. Am. Chem. Soc.* 1976, *98*, 4218.

[j] Robin, M. B.; Basch, H.; Kuebler, N. A.; Wiberg, K. B.; Ellison, G. B. *J. Chem. Phys.* 1969, *51*, 45.

[k] Doering, J. P. *J. Chem. Phys.* 1977, *67*, 4065.

[l] Chutjian, A. *J. Chem. Phys.* 1974, *61*, 4279.

[m] Reference 28. Experimental values for the triplet states[27,28] are not given since they have not yet been established unambiguously.[29]

[n] King, G. W.; Moule, D. *J. Mol. Spectrosc.* 1966, *20*, 331.

[o] Howe, J. A.; Goldstein, J. H. *J. Am. Chem. Soc.* 1958, *80*, 4846. Peaks of similar intensity at 3.40 and 3.71 eV.

states are well reproduced by the MNDOC PERTCI calculations, including the splitting of singlet and triplet states. If the energies are measured relative to the lowest excited state rather than relative to the ground state, the average absolute error in MNDOC energies is reduced to 0.29 eV (23 comparisons).[24]

From a methodical point of view, the MNDOC results in Table I indicate that the VO approximation is unreliable. It works well for π-π^* transitions in nonconjugated π systems, but otherwise yields results which differ appreciably from PERTCI emphasizing again the importance of electron correlation. The SELCI excitation energies, on the other hand, are quite close to the PERTCI ones, the average absolute deviation being only 0.14 eV. However, if there are differences, PERTCI is usually slightly superior to SELCI with regard to the spacing of excited states (cf. Table I). Therefore the simple SELCI treatment can be recommended only with caution.

The systematic underestimation of excitation energies in MNDOC can be ameliorated if the configuration space for the excited states is restricted to contain only single and double excitations relative to the closed-shell SCF configuration. Such a truncation has recently been suggested.[25] For the molecules studied, this leads to a fairly uniform increase of the MNDOC excitation energies, with no change in the sequences and very minor changes in the spacings of the excited states. The average absolute error in the MNDOC vertical excitation energies is reduced to 0.51 eV in this way. In spite of this improvement, we do not support such a truncation of the configuration space since it is incompatible with our general approach to the correlation problem[15,17] and since it will give unbalanced results for molecules of different size.[26]

Turning to individual molecules (cf. Table I), the largest MNDOC errors are found for ketene, regardless which of the proposed interpretations[27-29] of its UV spectrum is correct. This indicates that excited states of cumulenes might be problematic in MNDOC. On the other hand, relatively small errors are encountered with n–π^* transitions (cf. *trans*-glyoxal). This is probably due to the fact that the magnitude of the resonance parameter is less crucial for n–π^* than for π–π^* excitation energies.

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(25) Dick, B.; Hohlneicher, G. *Theor. Chim. Acta* **1979**, *53*, 221.

(26) Tavan, P.; Schulten, K. *J. Chem. Phys.* **1979**, *70*, 5407.

(27) Dixon, R. N.; Kirby, G. H. *Trans. Faraday Soc.* **1966**, *62*, 1406.

(28) Rabalais, J. W.; McDonald, J. M.; Scherr, V.; McGlynn, S. P. *Chem. Rev.* **1971**, *71*, 73.

(29) Laufer, A. H.; Keller, R. A. *J. Am. Chem. Soc.* **1971**, *93*, 61.

Table II. Adiabatic Excitation Energies (eV)

molecule	state[a]	MNDOC[b]	exptl	ref
C_2H_4	${}^1B_1$, N	1.94	2.82	*c, d*
	${}^3A_2$, T	2.05	(2.9)	*e*
	${}^1A_1$, Z	4.17		
	${}^1B_2$, V	4.34	(4.96)	*f, g*
C_2H_2	$\tilde{A}\ {}^1A_u$	4.82	5.23	*f*
HCN	$\tilde{A}\ {}^1A''$	5.77	6.48	*f*
	$2\ {}^1A'$	5.98	6.77	*f, h*
	$2\ {}^1A''$	6.59		
	$3\ {}^1A'$	7.19	8.14	*f, h*
$(CN)_2$	$\tilde{a}\ {}^3\Sigma_u^+$	3.64	4.13	*f*
	$\tilde{b}\ {}^3\Delta_u$	4.44	4.94	*i*
	$\tilde{A}\ {}^1\Sigma_u^-$	5.04	5.63	*i*
	$\tilde{B}\ {}^1\Delta_u$	5.41	5.99	*i*
CO_2	$A\ {}^1B_2$	4.54	5.70	*f*
CH_2O	$\tilde{a}\ {}^3A''$	2.47	3.12	*f*
	$\tilde{A}\ {}^1A''$	2.76	3.49	*f*
CH_2CO	$\tilde{a}\ {}^3A''$	1.29	2.39	*j, k*
	$\tilde{A}\ {}^1A''$	1.55	2.65	*j, k*
HCCCHO	$\tilde{a}\ {}^3A''$	2.58	2.99	*f*
	$\tilde{A}\ {}^1A''$	2.80	3.24	*f*
$(CHO)_2$	$\tilde{a}\ {}^3A_u$	2.10	2.38	*f*
	$\tilde{A}\ {}^1A_u$	2.35	2.72	*f*
HNO	$\tilde{a}\ {}^3A''$	0.85	0.85	*l*
	$\tilde{A}\ {}^1A''$	1.52	1.63	*f*

[a] Notation from ref 46 (for C_2H_4), 51 (for HCN), and 21 (otherwise). [b] Standard PERTCI except 2 MC for ${}^1A_1$, ${}^1B_2$ states of ethylene and all states of dicyan; half-electron MOs for ethylene. [c] Being the transition state for internal rotation, the ${}^1B_1$ state is a local minimum only in D_{2d} symmetry. [d] Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* 1955, *23*, 315. [e] Estimated by adding the calculated[46] singlet/triplet splitting of 0.1 eV to the experimental rotational barrier (footnotes *c* and *d*). [f] Reference 21. [g] A value of 5.77 eV (46 500 cm^{-1}) is given by: McDiarmid, R. *J. Chem. Phys.* 1971, *55*, 4669. [h] The assignment follows ref 51 (see text). [i] Bell, S.; Cartwright, G. J.; Fish, G. B.; O'Hare, D. O.; Ritchie, R. K.; Walsh, A. D.; Warsop, P. A. *J. Mol. Spectrosc.* 1969, *30*, 162. [j] Reference 29. [k] A previous interpretation[27] led to values of 2.65 and 3.21 eV. [l] Ishiwata, T.; Tanaka, I.; Akimoto, H. *J. Phys. Chem.* 1978, *82*, 1336.

The two lowest excited singlet states of *trans*-butadiene are of particular interest[25,30-32] since the ${}^1B_u$ state is dominated by a singly excited configuration whereas the ${}^1A_g$ state contains a large contribution from a doubly excited configuration (relative to the closed-shell SCF configuration). A recent electron impact study[33] suggests that the dipole forbidden ${}^1A_g$ state actually is the lowest singlet, in analogy to observations for larger polyenes.[34-36] This sequence cannot, of course, be obtained from a treatment which includes only single excitations, such as standard CNDO/S.[2] MNDOC produces this sequence if two main configurations are defined by the excitations $\pi_g \rightarrow \pi_g^*$ and $\pi_g\pi_g \rightarrow \pi_u^*\pi_u^*$ and if the configuration space is truncated at the double, triple, or quadruple excitation level relative to the closed-shell SCF configuration; the value in Table I refers to a space including triple excitations. The calculated relative energies of the two lowest singlets may be analyzed[25,32,37] in terms of the effective Coulomb interaction in the MNDOC model. The Dewar–Klopman–Ohno formula[38-40] used in MNDOC corresponds to an intermediate range of electron repulsion and is more appropriate than the short-range Mataga–Nishimoto[41] formula if correlation effects involve higher excited configurations.[25,32]

Table II lists MNDOC adiabatic excitation energies (term values) for 10 simple molecules. They are calculated as differences between the PERTCI energy of the respective excited state at its PERTCI optimized geometry and the BWEN energy of the ground state at its BWEN optimized geometry (see Tables VI and VIII of ref 15). Using the standard BWEN results for the ground state (rather than PERTCI ones) seems to be justified since the two sets of results differ only very slightly. The PERTCI geometry optimizations of the excited states are carried out by a modified Davidon–Fletcher–Powell method[42,43], which has been described in detail elsewhere.[44]

As expected, the adiabatic excitation energies by MNDOC show similar trends as the vertical ones. They are systematically too low, the average absolute error being 0.62 eV for 21 excitations studied. Again, the spacings between different excited states are reproduced much better, including various singlet/triplet splittings (cf. Table II).

Perpendicular ethylene is especially interesting because it presents one of the simplest examples of a biradicaloid system.[8] Note that the energy difference between the covalent and zwitterionic states is somewhat smaller in MNDOC than in the ab initio[45,46] case, the MNDOC energies themselves being generally too low. However, in accordance with the ab initio calculations[45,46] MNDOC predicts that the covalent singlet state is slightly more stable than the lowest triplet and that the zwitterionic Z state is slightly below the zwitterionic V state. In MNDOC, this PERTCI sequence of states is due to correlation effects since each of the two pairs of states is essentially degenerate at the SELCI level.

Table III shows the PERTCI optimized[44] geometries for 20 excited states, along with experimental and ab initio data. There have been some previous geometry optimizations of excited states in conjunction with semiempirical wave functions using either a single open-shell SCF configuration[12] or limited CI with singly excited configurations.[47-49] In several aspects, these previous results are similar to the present ones.

For all excited states studied, MNDOC predicts a qualitatively correct structure judging from the comparison with experiment (cf. C_2H_2, HCN, CO_2, CH_2O in Table III) or ab initio results (cf. HCN, CH_2CO in Table III). This is remarkable since the molecular shape in an excited state is often quite different from that in the ground state. In particular, the changes in bond lengths (cf. C_2H_2, $(CN)_2$, CO_2, CH_2O, HCCCHO, HNO in Table III) and bond angles (cf. C_2H_2, HCN, CO_2, CH_2O, HNO in Table III) upon excitation are usually reproduced very well by MNDOC.

Quantitatively, the average absolute error in bond lengths is 0.025 Å (21 comparisons), and in bond angles 5.8° (12 comparisons), with respect to experimental data. These MNDOC errors for excited states are higher than those for ground states (0.017 Å and 2.6°, respectively[15]) which is probably due to the fact that the minima in excited states are shallower than in ground states. Typically, MNDOC bond lengths between nonhydrogen atoms are slightly too small in excited states, and bond angles somewhat too large (see Table III). Nevertheless, the MNDOC structures of excited states seem accurate enough to be useful.

Turning to individual molecules, it is gratifying that geometry differences between various excited states are reproduced quite well by MNDOC (see, e.g., the CC bond length for C_2H_4, the

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Table III. Geometries of Excited States[a, b]

molecule	point group	state[c]	variable[d]	MNDOC[e]	exptl	ab initio[f]	ref
C_2H_4	D_{2d}	$^1B_1$, N	C–C	1.429		1.49	g, h
			C–H	1.090		(1.076)	
			HCH	117.1		(116.6)	
		$^3A_2$, T	C–C	1.423		1.49	h
			C–H	1.090		(1.076)	
			HCH	116.5		(116.6)	
		$^1A_1$, Z	C–C	1.339		1.40	h
			C–H	1.107		(1.076)	
			HCH	108.8		(116.6)	
		$^1B_2$, V	C–C	1.338		1.40	h
			C–H	1.106		(1.076)	
			HCH	109.1		(116.6)	
C_2H_2	C_{2h}	$\tilde{A}\,^1A_u$	C–C	1.368	1.388		i, j
			C–H	1.090			
			HCC	126.2	120	135	
HCN	C_s	$\tilde{A}\,^1A''$	C–N	1.294	1.297	1.318	i, k
			C–H	1.125	1.140	1.096	
			HCN	132.0	125.0	127.2	
		$2\,^1A'$	C–N	1.216	1.334	1.287	i, k
			C–H	1.171	(1.14)	1.102	
			HCN	117.2	114.5	124.9	
		$2\,^1A''$	C–N	1.284		1.316	k
			C–H	1.085		1.076	
			HCN	159.8		164.4	
		$3\,^1A'$	C–N	1.236		1.264	i,k
			C–H	1.089	(1.14)	1.092	
			HCN	153.6	141	141.2	
		$3\,^1A''$	C–N	1.195		1.229	k
			C–H	1.073		1.045	
			HCN	180.0		180.0	
		$4\,^1A'$	C–N	1.265		1.254	k
			C–H	1.263		1.313	
			HCN	180.0		180.0	
$(CN)_2$	$D_{\infty h}$	$\tilde{a}\,^3\Sigma_u^+$	C–N	1.246	1.224		l
			C–C	1.302	1.323		
CO_2	C_{2v}	$\tilde{A}\,^1B_2$	C–O	1.239	1.246		i
			OCO	133.9	122		
CH_2O	C_s	$\tilde{a}\,^3A''$	C–O	1.279	1.307	1.340	m, n
			C–H	1.111	1.096	1.078	
			HCH	113.3	(118.0)	119.7	
			$O{-}CH_2$	32.8	37.9	38.5	
		$\tilde{A}\,^1A''$	C–O	1.290	1.325	1.361	m, n
			C–H	1.102	1.095	1.077	
			HCH	114.8	118.0	120.0	
			$O{-}CH_2$	26.4	33.6	38.0	
CH_2CO	C_s	$\tilde{a}\,^3A''$	C–C	1.416		1.459	o
			C–O	1.202		1.200	
			$C{-}H_{cis}$	1.093		1.076	
			$C{-}H_{trans}$	1.085		1.076	
			CCO	140.2		131.7	
			CCH_{cis}	123.4		121.6	
			HCH	117.3		117.8	
		$\tilde{A}\,^1A''$	C–C	1.407		1.455	o
			C–O	1.198		1.201	
			$C{-}H_{cis}$	1.093		1.076	
			$C{-}H_{trans}$	1.089		1.076	
			CCO	142.9		130.9	
			CCH_{cis}	123.9			
			HCH	117.3		118.3	
$HC^1C^2C^3HO$	C_s	$\tilde{a}\,^3A''$	$C^1{-}C^2$	1.193	1.222		p
			$C^2{-}C^3$	1.412	1.397		
			$C^3{-}O$	1.298	1.310		
			$C^1{-}H$	1.062	1.060		
			$C^3{-}H$	1.100	1.112		
			$C^1C^2C^3$	177.4	178.2		
			C^2C^3O	121.6	118.1		
			C^2C^3H	119.8	121.0		
		$\tilde{A}\,^1A''$	$C^1{-}C^2$	1.195	1.238		i
			$C^2{-}C^3$	1.409			
			$C^3{-}O$	1.305	1.325		
			$C^1{-}H$	1.062			
			$C^3{-}H$	1.103	1.091		
			$C^1C^2C^3$	177.7			
			C^2C^3O	121.6			
			C^2C^3H	119.8			

Table III (*Continued*)

molecule	point group	state[c]	variable[d]	MNDOC[e]	exptl	ab initio[f]	ref
HNO	C_s	$\tilde{X}\,^1A'$	N-O	1.177	1.212		*i*
			N-H	1.035	1.063		
			HNO	114.9	108.6		
		$\tilde{A}\,^1A''$	N-O	1.191	1.241		*i*
			N-H	1.003	1.036		
			HNO	125.6	116.3		

[a] For ground-state geometries see Table VIII of ref 15 (except for HNO which is included here). [b] Values in parentheses have been assumed. [c] See footnote *a* of Table II. [d] Bond lengths A–B in Å, bond angles ABC in degree, angles A–BCD of A–B with plane BCD in degree. [e] See footnote *b* of Table II. [f] The ab initio papers quoted in the last column contain references to further ab initio studies. [g] See footnote *c* of Table II. [h] Reference 46. [i] Reference 21. [j] Demoulin, D. *Chem. Phys.* 1975, *11*, 329. [k] Reference 51. [l] Meyer, J. A.; Stedman, D. H.; Setser, D. W. *J. Mol. Spectrosc.* 1972, *44*, 206. [m] Jones, V. T.; Coon, J. B. *J. Mol. Spectrosc.* 1969, *31*, 137. [n] Bell, S. *Mol. Phys.* 1979, *37*, 225. [o] Dykstra, C. E.; Schaefer, H. F., III *J. Am. Chem. Soc.* 1976, *98*, 2689. [p] Lin, C. T.; Moule, D. C. *J. Mol. Spectrosc.* 1971, *38*, 136.

bond angle for HCN, or the O–CH_2 pyramidalization angle for CH_2O, in Table III). The MNDOC results for hydrogen cyanide are incompatible with the original assignment of the $\tilde{B}$ state[21,50] but support the recent reassignment based on an ab initio study.[51]

MNDOC SELCI structures are not included in Table III since they usually differ from the PERTCI ones only slightly. The deviations are similar to those found between the SCF and BWEN geometries of ground states.[15] In some cases, however, SELCI leads to qualitatively different structures predicting, e.g., a linear 2 $^1A''$ state of hydrogen cyanide as well as planar $\tilde{a}\ ^3A''$ and $\tilde{A}\ ^1A''$ states of formaldehyde. In the latter example, the correct pyramidal structures are obtained if open-shell half-electron RHF MOs[52] are used in SELCI, rather than the standard closed-shell RHF MOs. This indicates that the choice of the MO basis is more important in SELCI than in PERTCI.

Table IV lists dipole moments for pyramidalized perpendicular ethylene. This system provides the simplest example for the "sudden polarization" effect in zwitterionic excited states[53] which has prompted two recent ab initio studies.[46,54] To allow for reasonable comparisons, it was necessary to carry out the MNDOC calculations at the same geometries as the ab initio ones and make use of open-shell half-electron RHF MOs.

As noted previously,[46,54] it is not trivial to obtain a zero dipole moment for the D_{2d} perpendicular structure ($\alpha = 0°$) when approximate correlation treatments are used. This requirement of a zero dipole moment is fulfilled only in MNDOC CI calculations, which include all single and double excitations relative to the two degenerate main configurations ($T = 0$). The standard PERCI treatment with $T = 0.1$ eV is hopelessly wrong in this case, and is also unreliable for pyramidalized structures ($\alpha > 0°$). This is related to the fact that the matrix element between the two main configurations is extremely small in MNDOC which leads to an unbalanced SELCI vector for $T = 0.1$ eV; similar problems are encountered in the ab initio case (see 2e CI in ref 46). Hence, SELCI and PERTCI with a smaller threshold parameter, e.g., $T = 0.005$ eV, are to be used as approximate MNDOC correlation treatments which leads to much smaller deviations from the MNDOC CI reference results (see Table IV).

After these methodical preliminaries the MNDOC results in Table IV are easily interpreted. If the methyl group at C^1 is gradually pyramidalized while keeping the methylene group at C^2 planar, MNDOC obviously predicts a strong polarization and sizable dipole moments in the two zwitterionic states. C^1 bears the negative charge in the lower Z state, and C^2 in the higher V state, the charge separation between the two carbon atoms being of the order of 0.9–1.0 e at a pyramidalization angle of $\alpha = 20°$. The MNDOC dipole moments of the zwitterionic states increase strongly with pyramidalization (see Table IV), whereas the dipole moment of the covalent singlet state remains in the range 0.0–0.4 D. Judging from the published ab initio dipole moments,[46,54] which are, e.g., in the range 2.4–3.3 D for $\alpha = 20°$, the polarization in MNDOC is somewhat less strong and less sudden than in ab initio calculations, probably due to the higher flexibility of ab initio wave functions.

Table IV. MNDOC Dipole Moments (D) for the Z and V States of Pyramidalized Perpendicular Ethylene[a,b]

treatment	α[c]	Z state	V state
CI, $T = 0$	0	0.00	0.00
	10	0.60	0.57
	20	1.97	1.86
	30	2.81	2.56
SELCI, $T = 0.005$ eV	0	0.16	0.14
	10	0.76	0.75
	20	2.10	1.99
	30	2.89	2.63
PERTCI, $T = 0.005$ eV	0	0.13	0.14
	10	0.76	0.75
	20	2.07	1.96
	30	2.87	2.62
PERTCI, $T = 0.1$ eV	0	1.01	0.92
	10	2.80	2.74
	20	2.95	2.78
	30	3.14	2.80

[a] The dipole moment component along the CC bond has opposite signs in the two states (see text). [b] Geometry:[46,54] C–C 1.416 Å, C–H 1.076 Å, HCH 116.6°. [c] Pyramidalization angle α in degree, i.e., angle between C–C and the CH_2 plane.

The ethylene example thus indicates that MNDOC describes the polarization in zwitterionic states in a qualitatively correct manner. MNDOC SELCI calculations with intermediate threshold parameters (e.g., $T = 0.005$ eV) therefore provide a simple method to study polarization effects for larger molecules.[55] If a "sudden polarization" is found in this way, it is likely to persist in ab initio calculations which will tend to produce larger polarization effects.

Discussion

Dynamical complications being neglected, photochemical reactions are usually governed by the potential surfaces of the lowest excited singlet (S_1) and triplet (T_1), along with their relation to the ground-state surface (S_0).[8,56] A theoretical study of photochemical reactions will focus on locating minima, barriers, and funnels in these surfaces. Minima in S_1 and T_1 occur at two types of geometries: "spectroscopic minima" with structures similar to those of ground states and "biradicaloid minima" which correspond to ground-state species with two approximately nonbonding electrons. Funnels are regions with S_0–S_1 touching (or

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near touching) where the system can return to the ground state.[8,56]

A successful application of MNDOC to photochemical problems will thus require a reasonable description of these minima, barriers, and funnels. The presently available MNDOC results for excited states suggest the following preliminary assessment.

On the positive side, MNDOC treats S_1 and T_1 states with similar accuracy (see Tables I–III). Geometries of local minima are predicted reasonably well, both for "spectroscopic" and "biradicaloid" minima (see Table III). MNDOC is expected to provide a balanced description of different parts of the S_1 surface, including those parts where doubly excited configurations play an important role. For biradicaloid systems, MNDOC predicts the relative energies of covalent and zwitterionic states as well as the polarization in zwitterionic states in a qualitatively correct manner.

On the negative side, MNDOC energies and geometries are generally less accurate in excited states than in ground states. In particular, the excitation energies are systematically underestimated (cf. Tables I, II). This indicates that MNDOC will probably not predict funnels reliably especially in regions where the ground state is well represented by the closed-shell SCF configuration. Finally, no experience concerning MNDOC barriers in excited states is available yet.

On the basis of this evidence we believe that MNDOC can be applied in cautious explorations of excited-state surfaces. A more conclusive evaluation will only be possible after such applications have been carried out.

Future improvements of the MNDOC method should obviously attempt to correct for the systematic underestimation of excitation energies. For this purpose, excitation energies should be included as reference data in the parametrization procedure, rather than using ground-state data only. We have carried out some test calculations of this kind which suggest that better excitation energies can be obtained with modified MNDOC parameters but only at the expense of larger errors in the ground-state properties. An overall improvement of the MNDOC model would thus probably require the introduction of different parametric functions[11,15] rather than a mere variation of the MNDOC parameters.

Conclusions

MNDOC is superior to MNDO for the treatment of excited states, although the errors in MNDOC energies and geometries are larger for excited states than for ground states. Excitation energies are systematically underestimated by MNDOC, whereas energy differences between excited states, geometries, and charge distributions in excited states are reproduced reasonably. The present evidence supports cautions applications of MNDOC to photochemical problems.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (through a Liebigstipendium). The calculations were carried out on the TR 440 computer of the Universität Marburg.

Oxidation–Reduction Reactions of Complexes with Macrocyclic Ligands. Structure-Reactivity Relations and Reorganizational Barriers for Outer-Sphere Electron-Transfer Reactions of Low-Spin Cobalt(III)–Cobalt(II) Couples[1]

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Abstract: A series of structurally homologous *trans*-$Co(N_4)(OH_2)_2^{3+,2+}$ couples has been developed and used to probe the intrinsic, $\Delta G_{i,ab}^{\ddagger}$, and thermodynamic, ΔG_{ab}°, components of electron-transfer reactivity. X-ray structural studies have been used to determine that only the axial $Co–OH_2$ bond lengths change across the electron-transfer reaction coordinate. The equatorial Co–N (macrocycle) bond lengths are independent of formal oxidation state but do depend on the type of nitrogen donor (amine or imine) of the 14-membered macrocyclic ligands. Variations of self-exchange electron-transfer rates in this series are found to be attributable to the reorganizational energies which result from changes in metal–ligand axial bond lengths. However, the observed activation barriers are consistently larger than predicted only on the basis of Franck–Condon and work terms. The nearly constant discrepancy in these $\sigma^*–\sigma^*$ exchanging systems, $\Delta G^{\ddagger}(\text{obsd}) - \Delta G^{\ddagger}(\text{calcd}) \simeq 10$ kJ mol^{-1}, is attributed to a small value for the electron-exchange term (in a quantum mechanical formulation) or the electronic transmission factor (in a semiclassical formulation). Intrinsic parameters, $\Delta G_{i,aa}^{\ddagger}$, are determined for several $Co(N_4)(OH_2)_2^{3+,2+}$ couples, and these parameters are used to isolate the ΔG_{ab}° dependence of several cross reactions. It is found that $\Delta G_{ab}^{\ddagger}$ for cross reactions of these complexes depends on ΔG_{ab}° very nearly as predicted in the classical models developed by Marcus.

Introduction

The transfer of an electron between different complex ions with independent primary coordination spheres can occur at rates which span some 15–20 powers of ten.[2] On a molecular scale, these "outer-sphere" reactions approach a limit in which donor–acceptor interactions constitute an energetically insignificant perturbation

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(1) (a) Partial support of this research by the National Institutes of Health (Grant AM 14341) is gratefully acknowledged. (b) Presented in part at the 172nd National Meeting of the American Chemical Society, San Francisco, Calif, Sept 1976, INOR 168.

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0002-7863/81/1503-1431$01.25/0