

model transition states (6 and 7 for the carbonyl model or 8 and 9 for the enol model) for the compound of interest and enter the difference into the appropriate equation. For deprotonation with LDA in THF at -70°C , eq 1 would be used for the carbonyl model and eq 2 would be used for the enol model. Equations 18 and 19 would be used for the carbonyl and enol models, respectively, for deprotonation with LDA in a 77:23 (v/v) THF:HMPA solvent mixture at -70°C . If the group at R_2 is something other than methyl or ethyl, the carbonyl model would be used with the equations which include the steric parameter ν (eq 17 for LDA in THF and eq 20 for LDA in THF/HMPA).

The standard deviation of the correlations reflects both the uncertainty in the calculated energies and the variability in the observed enolate ratios due to minor differences in experimental technique. With the correlations in this work, predictions made using the carbonyl model should be accurate to within about 20% at the 95% confidence level. For the enol model, there can be no estimation of the error for eq 19, but predictions made with eq 2 would have an accuracy of about 20% at the 68% confidence level. It is anticipated that, as more data become available, both by experimentation and as more force field parameters are obtained, the correlations will gain strength and the uncertainty in the predictions will decrease.

The effect of cation-coordinating groups at R_1 and R_2 and the behavior of compounds with disubstitution at the acidic center have not been addressed in this work. One strength of the correlative approach is that new data can be incorporated into the model, and it is anticipated that the correlations can be adapted to accommodate these types of functionality as data permits.

Conclusion. The combination of force field modeling and regression analysis has proven to be a powerful probe into transition-state geometry which can potentially be applied to a wide variety of reactions. While the energies in this work were calculated exclusively with the MM2 program, the model energies

can, in principle, be calculated by any method of comparable accuracy. The force field calculations give detailed structural and thermodynamic information about the molecules being used as the transition-state models. Regression analysis then relates this information to the behavior of the reaction, and the resulting correlations have a number of uses. By comparison of the correlation equations with the theoretical behavior, the position of the transition state on the reaction coordinate and the presence of general factors not included in the model can be deduced. Examination of the points which do not follow the correlation can identify anomalous behavior due to unusual steric or electronic substituent effects, partial or complete equilibration, or errors in the computational method. The use of two models can minimize errors due to the latter. Finally, the correlations can be used as a predictive tool, with the standard deviation providing a measure of the reliability of the prediction.

The methods presented in this paper represent a fairly general approach to the investigation of regio- and stereoselective reactions. Preliminary effort with transition-state models for the aldol condensation have been successful, suggesting that the quantitative prediction of erythro:threo ratios is possible.⁴⁹

Acknowledgment. This research was supported by the National Institute of General Medical Sciences, U.S. Public Health Service (Grant GM 27320). The authors thank the Molecular Design Limited for a generous donation of computation time and for providing access to the use of their software packages. We also gratefully acknowledge the helpful consultation of Dr. Steven Peacock of Molecular Design Limited regarding the implementation of programs of the PRIME computer.

(49) Moreland, D. W., unpublished results. A different application of molecular mechanics to the study of the aldol transition state was reported recently: Dougherty, D. A. *Tetrahedron Lett.* 1982, 23, 4891.

Energies of Non-Kekulé Molecular States. Calculation by a Predictively Useful Semiempirical Method

Paul M. Lahti,[†] Angelo R. Rossi,*[†] and Jerome A. Berson*[†]

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511, and the University of Connecticut, Storrs, Connecticut 06268.
Received September 26, 1984

Abstract: The order and spacing of the lowest energy states of non-Kekulé molecules are reproduced by INDO/S-CI calculations. The results agree with those obtained from high-level *ab initio* calculations and with available experimental findings. State energy orders for a number of unknown non-Kekulé species are predicted. Hund's rule appears to be obeyed for large π -electron systems, although violations may occur for smaller molecules belonging to or closely related to the disjoint class. Good agreement also is found between the observed and INDO/S-CI calculated electron configurations (π vs. σ) of some doublet radicals. The method should be useful as a qualitative predictive tool.

The chemical and magnetic properties of non-Kekulé molecules are determined by the order and spacing of the lowest energy states. Attempts to predict the most stable spin and occupation pattern for the two (or more) frontier electrons require a decision on whether to invoke Hund's first rule, since the one-electron frontier orbitals are degenerate or nearly so.¹ This problem, adumbrated early in the history of molecular quantum mechanics,² has been brought into sharp focus recently by corollaries of approximate molecular orbital³ and valence bond⁴ arguments, which predict the possibility or even likelihood of violations of Hund's

rule in disjoint non-Kekulé systems. The experimental observation that such a violation does not occur in a specially constructed disjoint test system^{5d} provided one of the motivations for the present study, which aims to develop a more general basis for the prediction of the energies of non-Kekulé molecular states.

- (1) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* 1972, 11, 92.
- (2) Hückel, E. *Z. Phys. Chem. B* 1936, 34, 339.
- (3) (a) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* 1977, 99, 4587. (b) Kollmar, H.; Staemmler, V. *Theor. Chim. Acta* 1978, 48, 223.
- (4) (a) Ovchinnikov, A. A. *Theor. Chim. Acta* 1978, 47, 297. (b) Misurkin, I. A.; Ovchinnikov, A. A. *Russ. Chem. Rev. (Engl. Transl.)* 1977, 46, 967. (c) Klein, D. J. *Pure Appl. Chem.* 1983, 55, 299. (d) Klein, D. J.; Nelin, C. J.; Alexander, S.; Matsen, F. A. *J. Chem. Phys.* 1982, 77, 3101.

[†]Yale University.

*University of Connecticut.

A second problem that became acute during our experimental work^{5a-g} and that of others^{5h} arose from the initially surprising observation that heteroatom-for-carbon substitution in a non-Kekulé structure produced a molecule that had a high-spin ground state, despite the absence of a frontier orbital degeneracy in the energy levels derived from a single configuration theoretical treatment. In the case of *m*-quinomethane (7),^{5a} for example, the frontier orbitals are split by about 64 kcal/mol at the INDO level of calculation. One might reasonably have expected this to conduce to a closed-shell singlet ground state, but instead the experimental facts strongly suggest a triplet.^{5a-g}

An associated complication in heteroatom-substituted systems is the energy ordering of the high-spin states, n, π vs. all- π .

High-level ab initio methods involving large basis sets, geometry optimization, and extensive configuration interaction (CI) presumably would provide the most reliable answers to these questions. However, such calculations for large molecules, especially those containing heteroatoms, are still impractical.

We proposed instead to develop a semiempirical MO-CI computational algorithm that would reproduce the results of ab initio SCF-MO-CI techniques without their complexity and expense. Obviously, we did not hope to supersede state-of-the-art ab initio methods for quantitative calculations. Rather, the study might be viewed as a computational experiment, a search for a spin counterpart of simple Hückel theory. If successful, this might afford a utilitarian procedure for the construction of correlations and, perhaps more significantly, for the identification of synthetic targets of interest. We report here on the development of such a method, its calibration against experimental data and high-level ab initio results for small molecules, its successful application to the disjoint test molecule, and its extension to several unknown systems.

Semiempirical MO-CI theories such as PPP-CI⁶ and CNDO/S-CI⁷ have proven to be useful for the prediction of electronic spectral transitions. For the present purpose, it is necessary to distinguish triplet from open-shell singlet energies. We used the INDO⁸ approach, which is the lowest level of theory capable of this distinction.

At least three spectral INDO (INDO/S) parametrizations have been described.⁹ Zerner's scheme^{9c} has been thoroughly tested for ordinary Kekulé molecules and their excited states. Spectroscopic transitions, both $n-\pi^*$ and $\pi-\pi^*$, of both singlet and triplet species with and without heteroatoms have been properly described with this program. It is particularly useful that Zerner's program is parametrized to give good spectroscopic results when CI is included.¹¹ We hoped, therefore, that it would also be useful for the non-Kekulé systems, in which it is vitally necessary to describe the strong mixing of many configurations induced by orbital near-degeneracy.

Methods of Calculation. The calculations using a recent version of Zerner's INDO/S-CI program¹⁰ were carried out on an IBM 3081 at the University of Connecticut. For most compounds,

standard bond lengths and angles were assumed, although a few geometric optimizations were carried out at the INDO/1 level. All states were assumed to be planar, except for the trimethylenemethane (TMM) ${}^1B_1/{}^1B_2$ state. The energetic effect of twisting exocyclic C-C bonds in the systems treated here will be examined in a forthcoming paper. In general, the possibility of bond alternations was ignored. For bond parameters, all systems were assumed to be regular polygons except where noted in the tables: all methylene HCH angles = 120° , all r (CC) = 1.40 Å, r (CH) = 1.09 Å, r (CO) = 1.37 Å, unless otherwise noted. The reasons for such an arbitrary assignment of geometries are explained in the Results and Discussion section. Molecular orbitals for a given system at a given geometry were then obtained with Zerner's triplet spectroscopic parametrization, with coulomb integral weighting parameters $f_{oop} = 1.267$ and $f_{\pi\pi p} = 0.680$.^{9c} Unless stated otherwise, molecular orbitals obtained by the restricted open-shell Hartree-Fock (ROHF) method were used to generate the CI matrix for calculation, regardless of the CI multiplicity of the desired state. Triplet orbitals were used for both singlets and triplets, since in non-Kekulé systems of our type a proper description of the singlet MO's can be minimally correct only if it is a two-configuration SCF (TCSCF) description.¹¹ Triplet ROHF orbitals, which are usually very similar to singlet TCSCF orbitals, are qualitatively a much better SCF description of non-Kekulé molecular singlet states than single determinant restricted Hartree-Fock (RHF) orbitals. Of course, in the case where quintet states are energetically accessible, the choice of the multiplicity of the SCF-MO calculation is more complex, as we shall see later in this paper. Separate parametrization of singlet and triplet MO's for CI calculations, as others have similarly found,^{9b} gave inconsistent results for energies in manifolds of different multiplicities. Therefore we preferred the simplicity of using one set of MO's for all CI calculations at one fixed geometry, and eventually we found that use of MO's of the state of highest Kekulé bondedness gave satisfactory results.

Once MO's were available for a system of interest, the choice of the CI active orbital space is quite important, since the program available to us is limited to a 210×210 CI matrix. Again, in an attempt to be as self-consistent as possible, we chose the same sort of active space for all calculations. Each calculation included single excitations over the last nine doubly occupied orbitals (DOC's), the two singly occupied orbitals (SOMO's), and the first four virtual orbitals (VO's), plus double excitations over the last three DOC's, the two SOMO's, and the first two VO's. Many of the calculations were checked with smaller CI active spaces, and we found that the above level of CI was sufficient to stabilize state energies at our level of theory. Use of double excitations is at times questionable in semiempirical MO theories that include CI, due to the danger of counting interactions twice or of otherwise biasing the calculations in a way of which better CI functions would take account.^{9c,12} However, we found it vital for a proper description of singlet states to include double excitations, presumably because of the necessity for at least a TCSF wave function that includes double excitations, especially ionic configurations. For instance, when TMM was treated with single excitations only, the ${}^3A_2' \rightarrow {}^1A_1$ gap was 70 kcal/mol, while the use of double excitations in the INDO/S-CI calculation gave a gap of 28.4 kcal/mol, similar in magnitude to ab initio CI results for the same gap.¹³

Other details of the assumptions and parameters of INDO/S-CI are found in Zerner's work.^{9c} Some of the subroutines used in our work are not mentioned in the earlier references, since they

(5) (a) Rule, M.; Matlin, A. R.; Dougherty, D. A.; Hilinski, E. F.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5098. (b) Seeger, D. E.; Hilinski, E. F.; Berson, J. A. *Ibid.* **1981**, *103*, 720. (c) Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5144. (d) Seeger, D. E.; Berson, J. A. *Ibid.* **1983**, *105*, 5146. (e) Seeger, D. E.; Berson, J. A. *Ibid.*, in preparation. (f) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787. (g) Matlin, A. R.; Inglin, T. A.; Berson, J. A. *Ibid.* **1982**, *104*, 4954. (h) Platz, M. S.; Burns, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4425.

(6) (a) Flynn, C.; Michl, J. *J. Am. Chem. Soc.* **1974**, *96*, 3280. (b) Gisin, M.; Wirz, J. *Helv. Chim. Acta* **1983**, *66*, 1556. (c) Koutecký, J.; Doehner, D.; Wormer, P. E. S.; Paldus, J.; Čížek, J. *J. Chem. Phys.* **1984**, *80*, 2244.

(7) (a) Del Bene, J.; Jaffé, H. H. *J. Chem. Phys.* **1968**, *48*, 1807, 4050; **1968**, *49*, 1221. (b) Ellis, R. L.; Kuehnlenz, G.; Jaffé, H. H. *Theor. Chim. Acta* **1972**, *26*, 131.

(8) Cf. references in the following: Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.

(9) (a) Chen, S.-Y.; Hedges, R. M. *Theor. Chim. Acta* **1973**, *31*, 275. (b) Dick, B.; Nickel, B. *Chem. Phys.* **1983**, *78*, 1. (c) Ridley, J.; Zerner, M. *Theor. Chim. Acta* **1973**, *32*, 11; **1976**, *42*, 233.

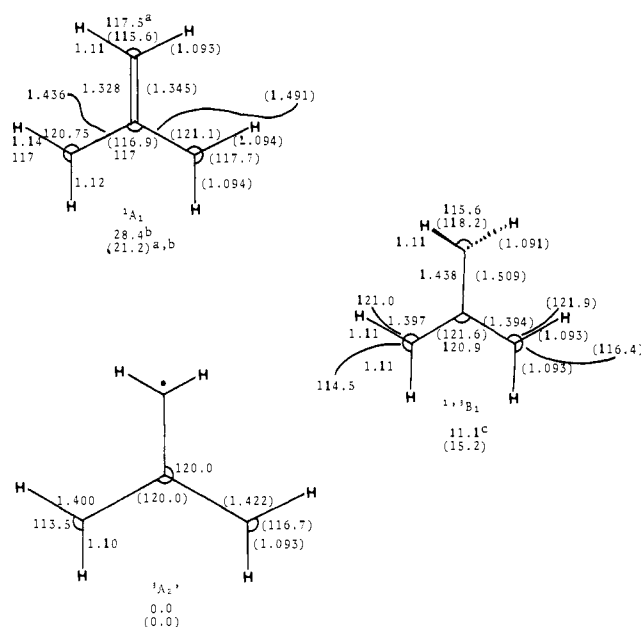
(10) We are grateful for Professor Zerner's kindness in making available to us a recent version of his group's program.

(11) Borden, W. T.; Davidson, E. R.; Feller, D. *Tetrahedron* **1982**, *38*, 737.

(12) (a) Schulten, K.; Ohmine, I.; Karplus, M. *J. Chem. Phys.* **1976**, *64*, 4422. (b) Schulten, K.; Karplus, M. *Chem. Phys. Lett.* **1972**, *14*, 305. (c) Birge, R. R.; Schulten, K.; Karplus, M. *Chem. Phys. Lett.* **1975**, *31*, 451.

(13) High-level computations for trimethylenemethane include the following: (a) Yarkony, D. R.; Schaeffer, H. F., III *J. Am. Chem. Soc.* **1974**, *96*, 3754. (b) Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1977**, *99*, 2053. (c) Davis, J. H.; Goddard, W. A., III *J. Am. Chem. Soc.* **1977**, *99*, 4242. (d) Dixon, D. A.; Foster, R.; Halgren, T. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 1359. (e) Dixon, D. A.; Dunning, T. H., Jr.; Eades, R. A.; Kleier, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 2878. (f) Auster, S. B.; Pitzer, R. M.; Platz, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 3812.

Chart I. Ab Initio and INDO/S-CI States for TMM



^a Parameters in parentheses are ab initio results from ref 13e, others are INDO/1, except for 1A_1 geometry, which is from ref 13f. ^b Energies in kcal/mol relative to the ground state. ^c INDO/S-CI 3B_1 energy at the same geometry was 10.1 kcal/mol.

are recent modifications of INDO/S-CI that were included in the program version we used.

Results and Discussion

Geometry Considerations. Trimethylenemethane (TMM) and Oxyallyl (OA). Our initial hope in this study was that the effect of geometry on qualitative state ordering would be small for most of the species of interest. We found this to be largely true, since these systems are mostly polycyclic aromatic compounds and hence fairly rigid. Partial optimization of states in this study made no qualitative difference in state orderings for *m*-xylylene, *m*-benzoquinomethane, and *m*-naphthoquinomethane. Therefore, we usually carried out calculations using the previously mentioned standard bond lengths and angles for systems that consisted of one or more fused rigid rings with exocyclic substituents. Our results with this approximation, as we shall see, turn out to be qualitatively very satisfactory. The resulting simplification of computation is in line with our desire that the method be as easy as possible while still being qualitatively correct.

For less rigid systems like TMM and oxyallyl (OA, **1b**), a small change of one geometric parameter has an effect on energy commensurately greater than it would in a larger system. Our approach to these small systems was therefore different. States for TMM and OA were optimized at the INDO/1 level of approximation⁸ with $f_{\sigma\sigma} = 1.00 = f_{\pi\pi}$. The resultant state geometries and INDO/S-CI energies are found in Charts I and II, along with corresponding ab initio results for each.

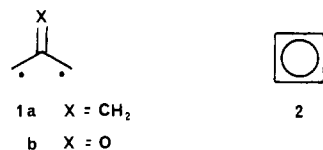
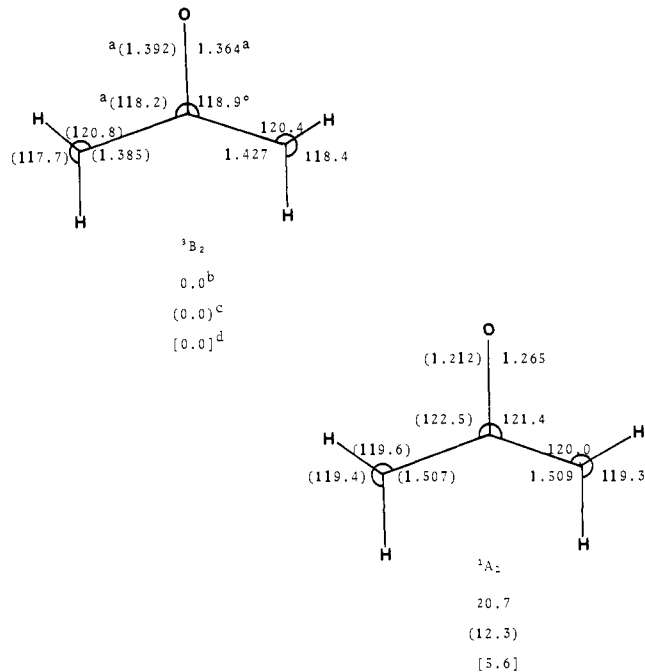


Chart II. Some Ab Initio Results for Oxyallyl



^a Geometric parameters from STO-3G basis sets. Bond lengths are in angstroms, angles in decimal degrees. Numbers in parentheses are for SCF/STO-3G (1A_1 is TCSCF), others are for MCSCF/STO-3G. Cf. also the results in ref 15b. ^b Energy in kcal/mol relative to the ground state. MCSCF/STO-3G optimized energy for this paper. ^c Energy in kcal/mol relative to the ground state. MCSCF/3-21G energies from ref 16b. ^d Energy in kcal/mol relative to the ground state. MCSCF/3-21G* energies from ref 16b.

INDO-S/CI 1A_1 state, which showed short bond lengths and artificially small angles.¹⁴ Surprisingly, the final INDO-S/CI energy, 19.0 kcal/mol, was in a reasonable range, despite the geometric distortion. We tried an ab initio geometry for this one state, to see if the energetic result would be improved despite our inability to obtain our own optimized geometry at the INDO/1 level. When the more appropriate geometry of Auster, Pitzer, and Platz^{15f} was used for the 1A_1 state, the ${}^3A_2' - {}^1A_1$ gap was 28.4 kcal/mol, which is still a close match to the ab initio energy gap. In sum, it would seem that even though the INDO/1 geometries were not particularly good for TMM (and OA, as we shall see), the state energies derived from INDO/1 geometries were still qualitatively correct.

n, π^* vs. π, π^* States. Oxyallyl. Calibrating ab initio multi-configurational SCF (MCSCF) calculations on oxyallyl (OA) were obtained by optimizing a 50-configuration CI wave function with regard to geometry,¹⁵ using the program GAMESS.¹⁶ A standard STO-3G¹⁷ basis set was used for all atoms. As Chart II shows, the use of an MCSCF wave function at the ab initio level makes an appreciable difference in geometric parameters, for reasons that have often been noted in high-level calculations.¹¹ The extreme shortness of the 1A_1 TCSCF/STO-3G C-O bond length

(14) The INDO/1 geometry for 1A_1 apparently collapses to a planar transition state for formation of methylenecyclopropane at our level of calculation, hence the necessity of assuming a geometry in this case. The internal CCC angle is only 64° in the INDO/1 geometry, with the equivalent HCH angles only 96° . Despite this distortion, the INDO/S-CI energy at this geometry is only 19.0 kcal/mol above the triplet ground state for TMM, in excellent agreement with the ab initio result of 21.2 kcal/mol.^{13e}

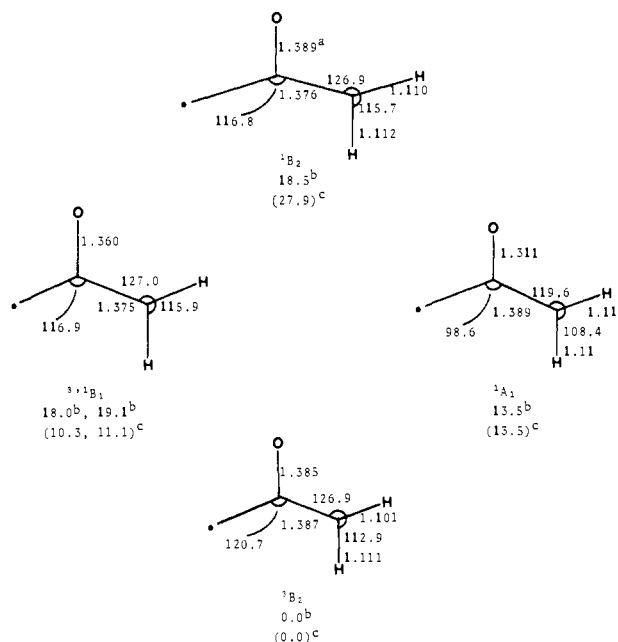
(15) (a) Similar calculations on OA at this level and at a higher level also have been carried out independently by others. Cf. ref 15b; (b) Osamura, Y.; Borden, W. T.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 5112. We are grateful to these authors for a preprint of their results prior to publication.

(16) Dupuis, M.; Spangler, D.; Wendelowski, J. J. "NRCC Software Catalog", 1980, Vol. 1, Program QG01 (GAMESS).

(17) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

The INDO/1 geometries for the ${}^3A_2'$ and 3,1B_1 states of TMM are in reasonable agreement with ab initio results.^{13e} The 1A_1 Jahn-Teller distorted state was not convergent on the C_{2v} geometry found by higher level calculations unless symmetry constraints were imposed on the optimization. This is not surprising, since TMM has been shown to require MCSCF optimization.¹³ When C_{2v} symmetry constraints were imposed, the 1A_1 geometry obtained was extremely distorted compared to MCSCF geometries. This was particularly noticeable in the "allyl" fragment of the

Chart III. INDO/S-CI States for Oxyallyl



^a INDO/1 geometries. ^b Energy relative to the ground state in kcal/mol for INDO/S-CI. ^c As in footnote ^b but at fixed geometry for all states $\rightarrow r(\text{CC}) = 1.40 \text{ \AA}$, $r(\text{CO}) = 1.35 \text{ \AA}$, $r(\text{CH}) = 1.09 \text{ \AA}$, all angles = 120° .

relative to the MCSCF/STO-3G length (1.212 Å vs. 1.265 Å) is particularly striking, as is the long ROHF-SCF 3B_2 C-O bond length relative to the MCSCF length (1.392 Å vs. 1.364 Å). Use of the MCSCF wave function avoids doublet instability in the single-determinant SCF wave functions, which is a well-established problem in SCF-calculations of this sort.¹⁸ Thus, the MCSCF results are computationally the better calibration mark.

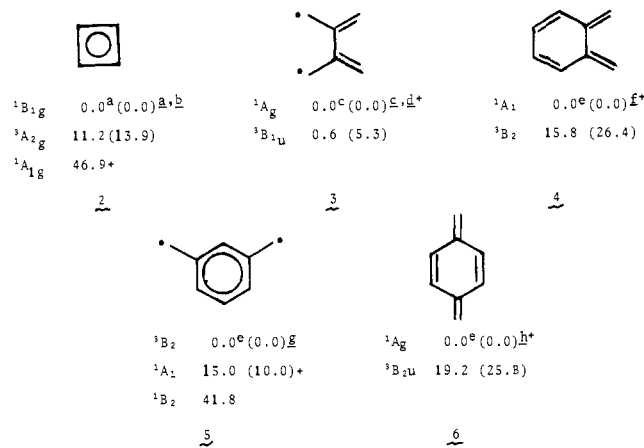
When oxygen atoms are present in the π framework, n, π^* states are added to the excited-state manifolds, a complication which is absent in the all-carbon analogue, TMM. MCSCF/STO-3G calculations find for OA a π, π^* 3B_2 ground state, with singlet and triplet n, π^* states about 6.2 kcal/mol higher in energy, followed next by the open-shell singlet π, π^* 1B_2 state at 18.4 kcal/mol, and finally by the closed-shell 1A_1 state 20.7 kcal/mol above the ground state (Chart II). These results are similar to ab initio results for TMM.

The INDO/S-CI results (Chart III) differ qualitatively from the MCSCF/STO-3G results. The INDO/1 geometries of Chart III were obtained with ROHF-type wave functions for open-shell states and used to obtain INDO/S MO's for CI as in TMM. The single-determinant RHF 1A_1 geometry is the worst by comparison to ab initio results.

Despite the problems with the geometries, the state energies are still useful, as is the case with TMM. The INDO/S-CI (Chart III) results show the π, π^* triplet 3B_2 to be the ground state, as was the case in the MCSCF/STO-3G calculation. However, they also show the 1A_1 state as the lowest singlet state of all, in contrast to the MCSCF/STO-3G calculation which gave 1B_1 as the lowest singlet. The close energetic spacing of n, π^* and excited singlet states at the INDO/S-CI level is also shown by calculations at a fixed oxyallyl geometry which gives a different excited-state ordering relative to the geometry-optimized results, since the close spacing of the states requires only small shifts to get qualitative state order inversions.

At first, we were concerned about the discrepancy between the INDO/S-CI and MCSCF/STO-3G results, but recent higher level calculations by Osamura, Borden, and Morokuma^{15b} on OA with MCSCF/3-21G and MCSCF/3-21G* wave functions are in excellent qualitative agreement with the INDO/S-CI results

Chart IV. INDO/S-CI Calibration Calculations



^a Geometry D_{4h} , $r(\text{CH}) = 1.09$, $r(\text{CC}) = 1.44 \text{ \AA}$. ^b Reference 6c. ^c Geometry D_{2h} , $r(\text{CH}) = 1.09$, $r(\text{CC}_{\text{allyl}}) = 1.36$, $r(\text{CC}_{\text{unique}}) = 1.50 \text{ \AA}$, all angles = 120° . ^d Reference 6c. ^e $r(\text{CH}) = 1.09$, $r(\text{CC}) = 1.40 \text{ \AA}$, all angles = 120° for INDO/S-CI. ^f Reference 25a. ^g Reference 24. ^h Reference 25a. ⁱ A plus sign (+) indicates a singlet of mostly closed shell character.

(compare results in Charts II and III). These calculations show that, although Hund's rule is still obeyed in OA, oxygen substitution stabilizes the closed-shell 1A_1 state relative to the analogous state in TMM so that 1A_1 is the lowest singlet for OA (instead of being the highest singlet, as the MCSCF/STO-3G results predict). The n, π^* states lie above 1A_1 , and the open-shell 1B_2 state is highest in energy. The INDO/S-CI results reproduce this trend quite well.

Hoffmann has pointed out that a SOMO gap of 1.5 eV is necessary at the extended Hückel level to cause a closed-shell system to be favored over an open-shell one.¹⁹ Similarly, in the case of OA the SOMO splitting is apparently still insufficient to produce a singlet ground state at the MCSCF/3-21G* level,^{15b} although the triplet-singlet splitting is reduced from that predicted by the calculation with an STO-3G basis set. Since the effects of higher level basis set and polarization functions are quite obvious in the ab initio calculations, the success of the INDO/S-CI calculations in this case is encouraging and is a tribute to the ability of a well-parameterized semiempirical method to overcome some of the problems of low-level ab initio methods. It bears repeating that although for oxyallyl the ab initio result requires geometry optimization, the INDO/S-CI calculation gives reasonable values even with an idealized geometry.

Other Calibration Calculations. Besides the calculations on TMM and OA, we also carried out calculations on cyclobutadiene (CB, 2), tetramethyleneethane (TME, 3), and the three isomeric xylylenes 4-6, as further calibration of the model. The INDO/S-CI state energies for these species are compared to appropriate literature values in Chart IV. The INDO/S-CI results agree quite well with other results.

Square-planar CB, predicted by one-electron theories (including INDO/S without CI) to be a ground-state triplet, is found to possess a ${}^1B_{1g}$ ground state 11.2 kcal/mol below the ${}^3A_{2g}$ state, in good agreement with high-level ab initio minimal basis set calculations, which put the singlet lower by 13-14 kcal/mol at the same geometry.^{20a,b} Small distortions from square-planar to rectangular geometry give a 1A_g ground state with a substantial drop (about 20 kcal/mol) in singlet energy, in qualitative agreement with the preference of rectangular over square-planar geometry by 8.3 kcal/mol found by double- ζ plus CI (DZ+CI)

(19) Hoffmann, R.; Zeiss, G. P.; van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.

(20) High-level computations for cyclobutadiene include the following: (a) Buenker, R. J.; Peyerimhoff, S. D. *J. Chem. Phys.* **1968**, *48*, 354. (b) Kollmar, H.; Staemmler, V. *Theor. Chim. Acta* **1978**, *48*, 223. (c) Borden, W. T.; Davidson, E. R.; Hart, P. *J. Am. Chem. Soc.* **1978**, *100*, 388.

Table I. INDO/S-CI State Energies for Some Benzenoid Non-Kekulé Systems

compd	state (energy ^a)	compd	state (energy ^a)
7	3A' (0.0)	14	3A1 (0.0)
	1A' (12.0) ⁺		1A1 (17.9) ⁺ ^b
	1A' (22.0)		3B1 (19.6) ⁺ ^b
	3A'' (22.9)*		1B1 (20.0)*
	1A'' (23.9)*		3B1 (21.6)*
			1B1 (21.7)*
			1A1 (29.4) ⁺
8	3A' (0.0)	11	3A' (0.0)
	1A' (17.0) ⁺		1A' (14.7) ⁺
	1A' (22.0)		1A' (34.3)
	1A'' (27.8)*		
	3A'' (28.0)*		
9	3B1 (0.0)	12	5A1 (0.0)
	1A1 (4.3) ⁺		3B1 (3.4)
	5A1 (10.1)		1A1 (9.4) ⁺
	3A1 (21.0)		3A1 (31.7)
	1A1 (29.3) ⁺		3B1 (32.1)
10	5A1 (0.0)	13	5A1 (0.0)
	3B1 (9.2)		3B2 (19.9)
	1A1 (22.6) ⁺		3A1 (36.9)
	5B1 (27.5)*		1A1 (42.9) ⁺

^a INDO/S-CI energies relative to the ground state in each system. Energies are in kcal/mol. ^b An asterisk denotes a state which is mostly of n, π^* character. A plus (+) indicates a singlet of mostly closed-shell character (small coefficients on open-shell configurations in the CI wave function).

calculations^{20c,21} and with experimental findings²².

For planar TME, INDO/S-CI calculations predict a singlet ($1A_g$) as the ground state, about 0.6 kcal/mol below the triplet ($3B_{1u}$), in reasonable agreement with Borden, Davidson, and Hart's SCF-MO-CI/STO-3G ab initio calculation,^{3a} which finds these two states to be in the same order and separated by 5.3 kcal/mol (at a fixed geometry).

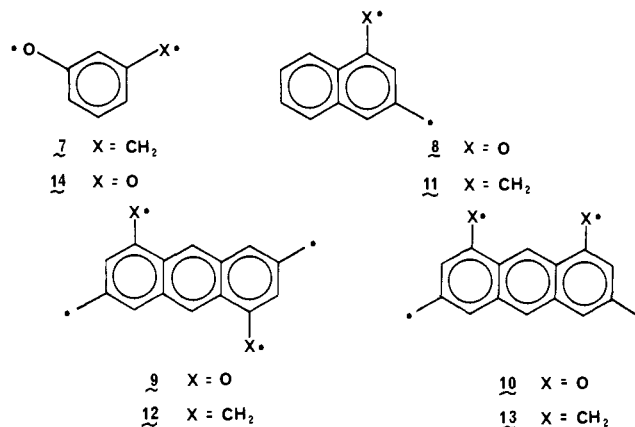
The cases of TME and CB are convincing examples of the necessity to include CI-derived dynamic spin-polarization effects^{3a,20c} in the systems of interest, for the results of our crude model are qualitatively correct with CI, while high-level SCF-MO results without CI are not. Thus, INDO/S-CI finds these systems in violation of Hund's first rule as usually formulated for molecular ground-state multiplicity, in agreement with ab initio CI theory. These correctly predicted violations are important, since we shall see that for other systems, INDO/S-CI correctly predicts experimental ground states where simpler qualitative theories based on these violations may fail to do so.

The three isomeric xylylenes (quinodimethanes), ortho,²³ meta,²⁴ and para,²⁵ are all known experimentally. Derivatives of the ortho and para isomers react as ground-state singlets, while the meta isomer appears to be a ground-state triplet,^{24a,c} as predicted by both simple HMO theory and by state-of-the-art ab initio calculations.²⁶ The INDO/S-CI results for all three species are shown in Chart IV, along with some previously published computational results. *o*- and *p*-xylylene are both predicted to be ground-state singlets by amounts comparable to other calculations.²⁷ *m*-Xylylene is found to have a $3B_2$ ground state 15.0

kcal/mol below a $1A_1$ excited state, in reasonable agreement with the $3B_2-1A_1$ gap of 10.0 kcal/mol found at a DZ+CI ab initio level by other workers.²⁶ The open-shell $1B_2$ state, as expected, as far higher in energy. Again, in this case the fairly rigid geometry of *m*-xylylene allows us to find a qualitatively correct answer without geometry optimization.

Thus, all of the calibration results obtained with our standard INDO/S-CI method were in qualitative agreement with high-level ab initio results. We therefore proceeded to test the model on systems less amenable to ab initio treatment.

Known Benzenoid Non-Kekulé Systems. A number of non-Kekulé systems predicted to have high-spin ground states have recently been characterized by ESR spectroscopy.^{5,28} We carried out INDO/S-CI calculations upon several of these systems, which are too large to be treated at reasonable expense by ab initio methods. *m*-Benzoquinomethane (7), *m*-naphthoquinomethane (8), and 3,7-dimethylenanthracene-1,5-dioxy (9) have all been shown experimentally to be ground-state triplets, while 3,6-dimethylenanthracene-1,8-dioxy (10) has been shown to be a ground-state quintet. It will be noted that high-spin ground states (in formal obedience to Hund's rule) are observed for these systems despite the already mentioned large splitting of the single configuration-derived frontier orbitals. Table I shows INDO/S-CI



state energies for these systems as well as for several systems derived by isoelectronic substitution of methylene for oxygen on 8-10 (11-13) and for *m*-quinone (14). For all the experimentally tested cases, INDO/S-CI predicts the observed ground-state multiplicity. In addition, the ground states for these species are predicted by a substantial gap to be all- π rather than n, π .

The correct finding of a triplet ground state for 9 is particularly interesting, since the experimental finding disagrees with the qualitative theories of Ovchinnikov^{4a,b} and of Borden and Davidson.^{3a} The Ovchinnikov theory specifies that, for an alternant system with n^* starred π centers and n^0 unstarred centers, the ground-state spin quantum number S_g will be

$$S_g = (n^* - n^0)/2$$

which for 9 predicts a singlet ground state, since the multiplicity is $2S_g + 1$. This formulation of S_g is supposed^{4a} to hold true regardless of perturbing heteroatom substitution. Borden and Davidson have formulated a similar qualitative theory whereby disjointness of the frontier one-electron MO's favors the possibility of a singlet ground state where a triplet might otherwise be expected. A system is disjoint if its molecular orbitals may be confined to completely non-overlapping sets of π centers. This minimizes the effect of the interelectronic repulsion that tends to destabilize π -conjugated singlets relative to triplets. Compound 9 turns out to be just such a disjoint system, and hence it is possible candidate for a singlet ground state. However, experimentally compound 9 obeys the Hund's rule based formulation of Longuet-Higgins²⁹ for a system with N π centers and T double bonds

(21) Borden, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 5968.

(22) (a) For a review and leading references see: Maier, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 425. (b) Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1980**, *102*, 4273.

(23) (a) Dolbier, W. R., Jr.; Matsue, K.; Dewey, H. J.; Horak, D. V.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 2136. (b) Miller, R. D.; Kolc, J.; Michl, J. *J. Am. Chem. Soc.* **1976**, *98*, 8510.

(24) (a) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 628. (b) Migiridicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400. (c) Goodman, J.; Berson, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 1867.

(25) (a) Errede, L. A.; Hoyt, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 436. (b) Williams, D. J.; Pearson, J. M.; Levy, M. *J. Am. Chem. Soc.* **1970**, *92*, 1436.

(26) Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 1791.

(27) (a) Döhnert, D.; Koutecký, J. *J. Am. Chem. Soc.* **1980**, *102*, 1789. (b) Baudet, J. *J. Chim. Phys.-Chim. Biol.* **1971**, *68*, 191.

(28) (a) Cf.: *Tetrahedron*, **1982**, *38*, 733 ff. (b) Inglin, T. A.; Matlin, A. R.; Berson, J. A. *J. Am. Chem. Soc.*, submitted.

in the Kekulé structure with maximum T , the ground-state multiplicity is predicted to be

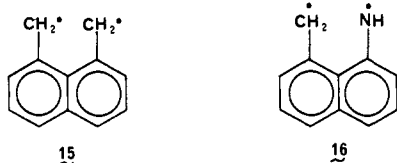
$$\text{multiplicity} = N - 2T + 1$$

We shall see that the Longuet-Higgins relationship and INDO/S-CI agree on predictions for other systems for which the other qualitative theories make different predictions. However, the Longuet-Higgins relationship fails for TME, whereas INDO/S-CI agrees with ab initio theory. Thus, INDO/S-CI appears to account for effects that cause all the qualitative models to fail in one case or another. Presumably the qualitative models overemphasize one characteristic affecting ground-state multiplicity to the exclusion of others and thus eventually give an incorrect result.

One question that needed to be resolved in the larger systems was the choice of a multiplicity for the SCF-INDO/S calculation to obtain MO's for the CI calculations. In the case of compounds **9** and **10**, use of either triplet or quintet orbitals gave the correct ground state. However, in the case of **9**, use of quintet orbitals gave a suspiciously low result for the ${}^3B_1-{}^5A_1$ gap, 2.4 kcal/mol vs. 10.1 kcal/mol with triplet MO's. We found also that use of quintet MO's for TME gave a triplet ground state 13.7 kcal/mol below the singlet, in contrast to the result with triplet MO's, for which a singlet ground state was found in agreement with ab initio calculations. This led us in later calculations to use triplet MO's for all systems save those where no Kekulé structure may be drawn with fewer than four unpaired electrons. In that case we used quintet MO's. Thus, use of MO's appropriate to the state with highest Kekulé bondedness seems appropriate for these systems, as mentioned earlier. This procedure gave reasonable results for all the rest of the systems in Table I. For instance, despite having a (suspicious) quintet ground state, hydrocarbon **12**, like the dioxy-substituted **9**, is also predicted to violate the qualitative expectations for disjoint systems by having a triplet below the singlet state.

In the larger benzenoid non-Kekulé systems, oxygen substitution has little effect on the order or energy spacing of the states (see the series **7-14**). The major change is the introduction of n,π states. Again, limited heteroatom substitution seems insufficient to overcome the tendency for larger systems to obey Hund's rule.

Generally, a form of Hund's first rule for molecules seems to be followed by the larger systems, in agreement with the Longuet-Higgins formulation of ground-state multiplicity, regardless of perturbing oxygen-for-methylene substitutions. This pseudo-Hund's rule seems to apply also to other systems which we did not study by INDO/S-CI, such as **15** and **16**, which are known experimentally to be ground-state triplets.³⁰ The usual criterion for application of Hund's rule is that the half-occupied one-electron frontier MO's should be degenerate or nearly so. Evidently, this criterion can be quite inadequate, as the present results show.

**15****16**

Some Non-Kekulé Systems of Uncertain Ground State. The success of INDO/S-CI on CB and TME, where the violations of Hund's rule seem to occur, led us to attempt the method on some borderline cases where the various qualitative theories clash, or where they are not applicable, in order to obtain results not easily obtained by ab initio theory.

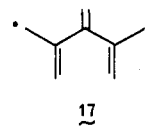
The planar system 2,3,4-trimethylenepentadienyl (**17**) is predicted by the method of Longuet-Higgins to be a ground-state triplet. The method of Ovchinnikov makes the same prediction since $n^* = 5$ and $n^o = 3$. However, the MO's of the system are confinable to disjoint atom sets. Borden and Davidson point out

Table II. INDO/S-CI State Energies for Systems of Uncertain Ground State

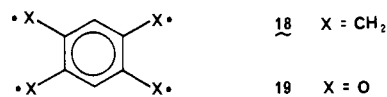
compd	state (energy ^a)	compd	state (energy ^a)	
17	3B2 (0.0)	18 ^b	3B3u (0.0)	
	1A1 (5.6) ⁺ c		1Ag (15.3) ⁺	
	1B2 (62.3)		3B2u (21.2)	
18	1Ag (0.0) ⁺	19 ^b	3B1g (21.4)	
	3B3u (9.0)		5Ag (29.3)	
	3B2u (42.4)		3B3u (0.0)	
	5Ag (51.0)		1B1g (0.1)	
	3B1g (54.0)		1Ag (6.5) ⁺	
19	3B3g (0.0)	20	3Ag (9.5) [*]	
	1Ag (1.1) ⁺		1Ag (10.0) [*]	
	3B3u (2.1) [*] c		21	3B3u (0.0) ^d
	1B3u (2.5) [*]			1A1 (0.2) ⁺
	3B3u (11.8) [*]			1A1 (5.4) ⁺
20	1B3u (12.2) [*]		3B1u (10.2) ^d	
	3B2 (0.0) ^d			
	1A1 (0.9) ⁺			
	3B1 (5.7) [*]			

^aINDO/S-CI energies relative to the ground state in each system. Energies are in kcal/mol. ^bState energies with quintet MO's instead of triplet MO's. ^cAn asterisk denotes a state which is mostly of n,π^* character, a plus (+) denotes a singlet mostly of closed-shell character. ^dDenotes an n,σ^* state, mostly of open-shell character.

that therefore **17** may be a ground-state singlet.^{3a} INDO/S-CI calculations show that planar C_{2v} **17** is a ground-state triplet, with an excited-state singlet 5.6 kcal/mol higher in energy (Table II). Although the parent system would have severe problems connected to requirements for planarity, derivatives of **17** may someday resolve the question of the ground state of this most unusual system.

**17**

Similarly, 1,2,4,5-tetramethylenebenzene (TMB, **18**) and its tetraoxy analogue, **19**, are non-Kekulé alternant, disjoint cases. In these cases the Ovchinnikov and the Borden-Davidson models agree that singlet ground states are favored. For TMB, use of our usual formula (triplet MO's for CI) gave a 1A_g ground state by 9.0 kcal/mol, in violation of Hund's rule and in agreement with the qualitative theories (Table II). Use of quintet MO's, however, reversed this ordering and gave a triplet ground state by 15.3 kcal/mol. This may, therefore, be a system of the right size^{31a} for the effects favoring violation of and obedience to Hund's rule to be nearly equally balanced.

**18****19**

As with TME, the triplet MO results in our INDO/S-CI calculations favor a singlet ground state for TMB. This result is confirmed at a more sophisticated level by an ab initio SCF-MO-CI calculation with geometry optimization, as is reported in another paper.^{31b}

INDO/S-CI calculations on 1,2,4,5-tetraoxybenzene **19**, using either triplet or quintet MO's, give triplet ground states nearly degenerate with singlet excited states. For this highly hetero-substituted molecule, there is a very high density of states up to 20 kcal/mol above the ground state (Table II). Note that the n,π^* states are a good deal lower in energy here than for less substituted examples. With so high a density of states one can most safely conclude from these calculations that **19** has the potential of being electronically very complex and that one cannot predict its ground state with even a modicum of confidence. This is an indicator of some of the dangers of applying simple qualitative

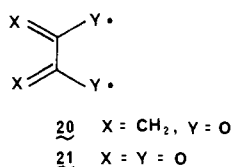
(29) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265.(30) (a) Pagni, R.; Burnett, M. N.; Dodd, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 1972. (b) Platz, M. S.; Burns, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4425.

Chart V. INDO/S-CI Results for Nonbenzenoid Non-Kekulé Systems^c

22	24	25	25
³ A'	³ B ₂	³ B ₂	³ B _{2u}
0.0 ^{a,b}	0.0 ^{a,b}	0.0 ^{a,b}	0.0 ^{a,b}
¹ A'	¹ A ₁	¹ A ₁	¹ A _g
12.7	18.9 ⁺	16.3 ⁺	24.1 ⁺
¹ A'	¹ B ₂	¹ B ₂	¹ B _{2u}
31.5 [*]	42.0	23.6	26.8
³ A''		³ B ₁	
41.7 [*]		42.6 [*]	
¹ A''		¹ B ₁	
42.0 [*]		44.7 [*]	

^a Relative energies above the ground state in kcal/mol. ^b The ring system is a regular octagon with $r(\text{CC}) = 1.40$ Å. All $r(\text{CH}) = 1.09$, $r(\text{CC}) = 1.35$. Methylene HCH = 120° . ^c An asterisk (*) denotes an n, π^* state. A plus (+) denotes a singlet of mostly closed shell character.

arguments to predict ground states of molecules with multiple heteroatom substitution, especially in smaller systems. Indeed, substitution of two to four oxygens on TME gave predominantly n, π^* triplet ground states nearly degenerate with configurationally mixed singlets. Apparently, in smaller molecules n, π^* and n, σ^* states become more favorable as the number of available n-orbitals grows. The results for the oxy-substituted TME's **20** and **21** are included with the results for TMB and for **19**.



Potential Nonbenzenoid Non-Kekulé Cyclic Systems. One of the questions that interested users of early MO theory was whether planar cyclooctatetraene (COT) is antiaromatic, since it is a $4n$ annulene. Although this question is seemingly without satisfactory experimental resolution because COT is nonplanar, simple Hückel theory led to correct predictions of planar, aromatic COT dication^{32a,b} and dianions.^{32c} If the related non-Kekulé, nonbenzenoid systems 1-methylenecyclooctatetraene-3-oxo (**22**) and 1-methylenecyclooctatetraene-5-oxo (**23**) are flat, simple HMO theory indicates that the oxygen substitution on **22** and **23** would break the frontier NBMO degeneracy, favoring a singlet at the one-electron level. However, the method of Ovchinnikov unequivocally predicts both **22** and **23** to be ground-state triplets. INDO/S-CI calculations on planar species **22** and **23** and their planar all-hydrocarbon counterparts **24** and **25** are listed in Chart V. All the COT derivatives are found to be triplets by substantial margins at this level of theory. Of course, this does not answer the question of whether the species should be planar, but the model at least agrees well with the results expected on the basis of the qualitative model and upon the trend in this study that limited oxygen substitution in a hydrocarbon ground-state triplet system

(31) (a) A referee of this paper and also Professor W. T. Borden have pointed out that the breakdown of the predictions based on disjoint character may not be a result of the size of the π -system per se but instead may be a secondary consequence of size which results from the additional connectivity channels available in large, ramified π -systems. This seems likely to perturb the TME-like connectivity that lies at the heart of the disjoint model. It may be relevant to report that, at the suggestion of Professor Borden, we have carried out an INDO/S-CI calculation on the disjoint molecule obtained by conceptually disconnecting bonds C₁-C₁₁ and C₅-C₁₄ of the anthracene system of **9**. This species behaves like a true disjoint case and is predicted to be a ground-state singlet. (b) Lahti, P. M.; Rossi, A.; Berson, J. A. *J. Am. Chem. Soc.*, submitted.

(32) (a) Olah, G. A.; Staral, J. S.; Paquette, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 1267. (b) Olah, G. A.; Staral, J. S.; Liang, G.; Paquette, L. A.; Melaga, W. P.; Carmody, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 3349. (c) Katz, T. J. *J. Am. Chem. Soc.* **1960**, *82*, 3784.

Chart VI. INDO/S-CI Results for Non-Kekulé, Nonalternant Systems^d

26	27	28	29
³ B ₂	¹ A ₁	³ B ₂	¹ A ₁
0.0 ^{a,b}	0.0 ^{a,b*}	0.0 ^{a,b}	0.0 ^{a,b*}
¹ A ₁	³ B ₂	¹ A ₁	³ B ₂
14.2 [*]	0.1	12.1 [*]	1.0
³ B ₂	³ B ₁	³ B ₂	³ B ₁
34.9	48.0 [*]	31.5	30.8 [*]
	¹ B ₁		51.2 [*]
	¹ B ₂		38.8
³ A''			
0.0 ^{a,c*}	³ A''		
0.5	0.0 ^{a,c}		
	¹ A''		
	13.3 [*]		

^a All energies in kcal/mol relative to the ground state. ^b The ring portion is a regular polygon with $r(\text{CC}) = 1.40$ Å. All external substituents bisect external angles. All CH₂ have angles of HCH = 120° . All exocyclic $r(\text{CC}) = 1.40$ Å, except for unique CH₂, which has $r(\text{CC}) = 1.365$ Å, $r(\text{CH}) = 1.09$ Å. The molecule is planar. ^c The ring portion has $r(\text{CH}) = 1.09$ Å, $r(\text{CC}) = 1.40$ (1.386 unique CC) Å. All external substituents bisect external angles. Methylene angle of HCH = 120° , $r(\text{CC}) = 1.40$ Å. ^d An asterisk (*) denotes an n, π^* state. A plus (+) denotes a singlet of mostly closed shell character.

Chart VII. INDO/S-CI State Energies for Conjugated Radicals

32	33	34
² B ₁	² B ₂	² B ₂
0.0 ^a	0.0 ^{a,b} (0.0) ^c	0.0 ^a (5.3) ^d
² B ₂	² A ₂	² A ₁
23.6	18.0 (6.2)	23.0 (30.0)
² A ₂	² A ₁	² A ₂
63.0	19.6 (6.9)	29.5 (0.0)

^a INDO/S-CI energies in kcal/mol relative to the ground state.

^b INDO calculation uses $r(\text{CH}) = 1.08$ Å, $r(\text{CO}) = 1.262$ Å, angle OCO = 114° . ^c Reference 33. ^d Reference 34.

does not generally favor the singlet to any major extent, contrary to simple HMO expectations. Thus, once again Hund's rule is followed.

We then applied our model to nonbenzenoid, nonalternant systems **26–31** (Chart VI), which are not amenable to analysis by the Ovchinnikov or Longuet-Higgins formulations. For hydrocarbons **26** and **28**, a triplet ground state is predicted to be strongly favored. This agrees with application of Hund's rule to the simple HMO result, which shows degenerate half-filled frontier orbitals for both.

In **27** and **29**, where oxygen has been substituted for the unique methylene, INDO/S-CI predicts a near-degeneracy of singlet and triplet states. The synthesis of these species thus would be not only an experimental challenge but a fascinating test of the predictions of INDO/S-CI.

In the case of the furan compounds **30** and **31**, it appears that the aromatic heterocycle does not alter the state orderings that would obtain if these species were considered to be merely a weakly perturbed TME and vinyl TMM, respectively. Compound **30** possesses a ground-state singlet 0.5 kcal/mol below an excited triplet, which is a result nearly identical with that for the simple

parent TME system. Compound **31** has a ground-state triplet 13.5 kcal/mol below its lowest singlet, which is very similar to the TMM result. Thus these systems and their isoelectronic pyrrole and thiophene analogues are intriguing experimental targets to test the INDO/S-CI predictions.

Radical Species. We also used our model to carry out INDO/S-CI calculations on phenoxy (**32**), formyloxy (**33**), and benzoyloxy (**34**). Although other semiempirical methods exist for finding spectral transition energies for radical species—such as the CNDO/S-CI method³³—we were curious to see how INDO/S-CI performed for odd-electron species. MO's were obtained with use of ROHF-INDO/S doublet calculations. The CI active space included the last 6 DOC's, the SOMO, and the first 5 VO's for single excitations and 3 DOC's, the SOMO, and the first 3 VO's for double excitations. The results and comparison to other literature calculations are listed in Chart VII.

Phenoxy is found to possess a 2B_1 ground state, with the unpaired electron in a π orbital. This is consistent with experimental interpretation of the ESR hyperfine data for phenoxy derivatives as indicating a π radical.³⁴ Formyloxy is found to give the same state ordering as found for geometry-optimized MCSCF calculations,³⁵ with the $\sigma {}^2B_2$ state lowest. The INDO/S results were not geometry optimized, despite the findings of the MCSCF study that there is geometry variation among the states; in this case use of a fairly typical geometry for all the states was sufficient to give qualitative agreement with the MCSCF result. Similarly, fixed geometry calculations of benzoyloxy give a planar $\sigma {}^2B_2$ state about 1.0 eV below the π radical and another σ radical. This result is contrary to the ab initio SCF results obtained without CI,³⁶ but it is consistent with the MCSCF results for formyloxy and with experimental results by McBride and Merrill.³⁷ The INDO/S-CI calculation shows the planar 2B_2 state to be at a minimum with respect to torsion of the carboxylate group with fixed bond lengths and angles. The barrier was found to be 1.5 kcal/mol at this level of theory, with the bisected form at the top of the barrier. Thus INDO/S-CI appears to be useful for qualitative evaluation of odd- as well as even-electron radical-state ordering.

Tetramethylenemethane, a Nonconjugated Polyradical. The sole nonconjugated system treated in this study was tetramethylenemethane (**35**). Recent ab initio calculations³⁸ predict a



(33) Jaffé, H. H.; Chang, H. M.; Masmanidis, C. A. *J. Comput. Phys.* **1974**, *14*, 180.

(34) (a) Broze, M.; Luz, Z.; Silver, B. L. *J. Am. Phys.* **1967**, *46*, 4891. (b) Rieker, A.; Scheffler, K. *Tetrahedron Lett.* **1965**, 1337.

(35) Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 1459.

(36) Pacansky, J.; Brown, D. W. *J. Phys. Chem.* **1983**, *87*, 1553.

(37) McBride, J. M.; Merrill, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1723.

ground-state singlet ~ 2 kcal/mol below the lowest excited triplet state. INDO/S-CI calculations using the ab initio geometry and quintet MO's similarly show a ground-state singlet 3.7 kcal/mol below the excited 3A_2 state. Use of triplet MO's for the INDO/S-CI calculations, however, gave a ground-state 3A_2 by 15 kcal/mol. These results support the use of MO's for the multiplicity of highest Kekulé bondedness for INDO/S-CI calculations and imply that spiro-conjugated systems may also be qualitatively well-described by INDO/S-CI.

Conclusions

INDO/S-CI accomplishes extremely well the general goals of our study. For large rigid systems, use of one set of standard bond lengths and angles and one set of MO's, as determined by the precepts set forth earlier, seems to give satisfactory results, thus decreasing the number of computations necessary. Use of a systematically chosen CI active space serves to standardize the calculations and further decrease complexity, especially since the maximum amount of CI available in Zerner's program seems more than sufficient to stabilize state energies at the single plus double excitation level. The method is also sufficiently flexible to permit partial geometry optimization at the SCF-INDO/1 level, if this is necessary. Heteroatom substituted systems may be treated as well as hydrocarbons. Most important, the cases we have studied gave INDO/S-CI results that are qualitatively confirmed by both theory and experiment where such data are available. In fact, INDO/S-CI concurs with experiment in some cases where simpler theoretical expectations are not realized. The method seems genuinely useful for qualitative predictions, despite its many approximations and assumptions. In this respect, its use in the prediction of spin properties of conjugated non-Kekulé molecules may be viewed as analogous to that of simple Hückel theory in the prediction of relative stabilities of conjugated Kekulé molecules.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-8011399) and the National Institutes of Health (GM 30787) for support of this research. We are also grateful to the University of Connecticut Department of University Computer Systems for a large grant of computer time. Professor W. T. Borden kindly provided helpful discussion and information in advance of publication, and Professor M. C. Zerner generously made available a recent version of his INDO/S-CI program.

Registry No. **1a**, 13001-05-3; **1b**, 17440-65-2; **2**, 1120-53-2; **3**, 16893-57-5; **4**, 32796-95-5; **5**, 32714-83-3; **6**, 502-86-3; **7**, 71946-86-6; **8**, 76984-35-5; **9**, 95406-52-3; **10**, 86392-78-1; **11**, 88017-91-8; **12**, 95406-53-4; **13**, 95406-54-5; **14**, 71946-90-2; **17**, 95406-55-6; **18**, 95406-56-7; **19**, 95406-57-8; **20**, 95406-58-9; **21**, 59263-82-0; **22**, 95406-59-0; **23**, 95406-61-4; **24**, 95406-60-3; **25**, 95406-62-5; **26**, 95406-63-6; **27**, 95406-64-7; **28**, 55524-32-8; **29**, 95406-65-8; **30**, 95406-66-9; **31**, 95406-67-0; **32**, 2122-46-5; **33**, 16499-21-1; **34**, 1854-28-0.

(38) McElwee-White, L.; Goddard, W. A., III; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 3461.