An Addendum to a Recent Paper by Halgren, Lipscomb, and Their Co-workers Concerning the Relative Accuracies of Several Current MO Methods

Michael J. S. Dewar* and George P. Ford

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received December 15, 1978*

Abstract: The results of MNDO semiempirical molecular orbital calculations are compared with a standard set of test data previously suggested for the evaluation of currently employed MO procedures by Halgren, Lipscomb, and their co-workers. The MNDO calculations which, for a single SCF cycle, require approximately the same computation time as CNDO/2 (geometry optimizations require ~1.5 SCF per variable) are 16 times more accurate than the latter method and about 3 times more accurate than PRDDO, STO-3G, or minimum basis set ab initio methods for the calculation of relative energies (MNDO calculation including geometry optimization; others at experimental geometries). For ionization potentials and dipole moments all methods perform similarly with the exception of CNDO/2, which is ~two and ~four times less accurate in the two cases.

Introduction

In a recent article in this journal Halgren, Lipscomb, and their co-workers[1] have presented a much-needed comparison of the accuracies and computational speeds of most of the current molecular orbital methods (CNDO/2, INDO, PRDDO, STO-3G, and others). Since the focus of these authors was on the methods which attempt to mimic the results of minimum basis set (MBS) ab initio calculations, the semiempirical methods developed in these laboratories, namely, MINDO/3[3] and MNDO,[3] were not included in this comparison. This omission seems unfortunate because the primary criterion of theoretical procedures in chemistry should be their ability to reproduce experiment rather than to mimic one another and because, as will be seen presently, the results given by our procedures are at least competitive in this sense. Indeed, they are now being very widely used by organic chemists; within 2 years of its introduction MINDO/3 was already the second most frequently requested program at QCPE.[4] We therefore felt that it would be of value to extend the comparisons of Halgren et al.[1] to include corresponding results for MNDO, this having been shown to be superior in almost every respect to its predecessor, MINDO/3.

The comparisons made by Halgren et al.[1] were based on a series of 11 organic molecules and 16 boron hydrides, carboranes, and borohydride anions. While Halgren et al. also cited experimental results, their main objective was to investigate the ability of semiempirical methods, in particular PRDDO,[5] to reproduce the results given by ab initio calculations. Their use of the term "accuracy" in their final conclusions referred to this aspect rather than ability to reproduce experiment.

As is well-known but infrequently documented, atoms and molecules are always calculated to be too unstable by the Hartree-Fock (HF) method, owing to the neglect of electron correlation inherent in the HF approximation. This deficiency is illustrated in Table I by a comparison with experiment of the total energies, given by the near-HF calculations of Snyder and Basch,[8] for some of the species discussed by Halgren et al. It will be seen that the errors are enormous by chemical standards, those in the case of molecules being comparable with the entire heat of atomization (ΔH_a, Table I). Unless these errors cancel in comparing the energy of a molecule with that of its constituent atoms, corresponding errors will appear in calculated heats of formation of molecules. As the results in Table I show, these[9] again are very large indeed by chemical standards, amounting to hundreds of kcal/mol even in the case of quite small molecules. Similar problems then arise in comparisons of energies of molecules derived from the same set of atoms, e.g., in calculations of heats of reaction or activation energies. It is clear that these cannot be usefully estimated by the HF method, still less by approximate revisions of it, except in an empirical sense, in areas where comparison with experiment has shown the results to be satisfactory, due to an unpredictable cancellation of errors. Attempts to circumvent this limitation by calculating correlation energies have so far been unsuccessful. The best approaches of this kind recover at most 80% of the correlation energy,[10] leaving errors that are still unacceptably large by chemical standards.

The HF method cannot reproduce heats of reaction for processes involving bond dissociation. Extensive tests by Pople have shown that treatments using minimum basis sets (e.g., STO-3G) failed likewise for reactions involving any changes of bond type (cf).[11] Larger basis sets, of double ζ type (e.g., 4-31G), including polarization functions (e.g., 6-31G*), also fail in certain cases, in particular for reactions involving species with multicenter bonds (e.g., $2BH_3 \rightarrow B_2H_6$).[12] Comparisons of the results from semiempirical treatments with those from ab initio calculations are therefore of limited chemical significance. We have therefore confined our attention here to comparisons of the methods cited by Halgren et al.[1] with MNDO and experiment.

Results

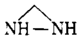
Energies. MNDO has the advantage of containing a semiempirical correction for electron correlation, enabling it to reproduce heats of formation with reasonable accuracy. This is illustrated by the comparisons shown in Table I. The root mean square error in the MNDO heats of formation for the present series of compounds was 9.4 kcal/mol, in between the values[3,13] for HCNO compounds and compounds containing boron.

Table II shows MNDO values for heats of reaction for the formal reaction processes considered by Halgren et al.,[1] together with experimental values where available. Table III compares the standard deviations of the MNDO values from experiment with corresponding values for the other procedures[1] in question. Note that the MNDO error is much smaller than that for the other procedures (except that used by Snyder and Basch, which was only a little less accurate). Note in particular the marked superiority of MNDO over 4-31G, a double ζ basis set which has frequently been used to estimate molecular energies.

It should also be noted that the calculations reported by

0002-7863/79/1501-5558$01.00/0

Table I. Comparison of Theoretical and Experimental Heats of Formation, Ionization Potentials, and Dipole[a-c]

	ΔH_a[d]	total energy		ΔH_f			IP, eV[h]		μ, D	
	exptl	Snyder-Basch[e]	exptl[f]	Snyder-Basch[e,g]	MNDO	exptl	MNDO	exptl	MNDO	exptl
B_2H_6	569.8	−33 112.1	−33 387.6	124.5	−1.8	8.4[i]	12.78	12.00		
B_4H_{10}					10.2	15.6[i]	12.50	10.39	1.30	0.56
B_5H_9					31.3	17.5[i]	11.48	10.50	2.97	2.13
B_5H_{11}					15.2	24.3[i]	12.02	10.31	2.33	
B_6H_{10}					18.8	22.2[i]	10.94	9.33	2.96	
1,2-$C_2B_4H_6$					62.3		11.36		2.25	1.50
4,5-$C_2B_4H_8$					33.6[j]		10.57[j]		1.14[j]	
2,4-$C_2B_5H_7$					33.7		11.61	10.94[k,l]	1.24	1.32
B_8H_{12}					26.2		10.80		3.63	
B_9H_{15}					25.9		11.24		3.61	
$B_{10}H_{14}$					16.7	7.1[i]	11.29	10.15[k,m]	4.08	~3.4
H_2	104.2	−707.0	− 731.2	23.9	0.7	0.0	15.74	15.98		
$HC{\equiv}CH$	391.7	−48 187.7	−48 513.3	175.6	57.3	54.3	11.03	11.40		
$H_2C{=}CH_2$	537.7	−48 949.2	−49 286.3	144.9	15.3	12.5	10.18	10.51		
$H_2C{=}C{=}CH_2$	675.5	−72 678.4	−73 171.4	231.9	43.8	45.6	10.02	10.07		
	812.6	−73 424.9	−73 935.5	216.3	11.2	12.7	11.43	11.0		
CH_3CN	590.2	−82 748.1	−83 284.6	223.7	18.9	20.9	12.80	12.21	2.63	3.92
CH_3NC	575.5	−82 730.9	−83 269.9	240.9	60.0	35.6	12.25[n]	11.27	2.17	3.85
$H_2C{=}N{=}N$	430.1	−92 727.3	−93 329.1	305.9	67.1	71	8.67[n]		1.25	1.50
	422.1	−92 701.2	−93 321.1	332.0	72.5	79	11.62[n]	10.75	1.55	1.59
		−93 400.5		363.6	45.7[o]		11.09[o]		1.39[o]	
	944.3	−97 131.6	−97 814.5	325.8	64.0	51.9	10.00[n]		0.41	0.68
	970.2	−97 179.2	−97 840.4	278.2	28.9	26.0	9.14	9.08		

[a] These data extend the comparisons of Table V, VII, XI, and XIV of ref 1; experimental values are from this source unless noted otherwise. [b] MNDO data for boron compounds are from ref 3c and M. J. S. Dewar and M. L. McKee, *Inorg. Chem.*, **17**, 1569 (1978); others are from ref 3b. [c] All energies in kcal/mol. [d] Heat of atomization calculated from $\Delta H_a = \Sigma\, \Delta H_f{}^A - \Delta H_f$ where $\Delta H_f{}^A$ are the heats of formation of the gaseous atoms at 25 °C from D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 37.** "JANAF Thermochemical Tables". 2nd ed. [e] Double ζ ab initio calculation from ref 8. [f] The total energy change for the formation of the molecule at 25 °C from the separated atoms and nuclei calculated as $E^{mol} = -\Sigma I_P{}^A - \Sigma\Delta H_f{}^A + \Delta H_f$. $I_p{}^A$ is the energy required to completely ionize each atom calculated by summing the individual ionization energies from "CRC Handbook of Chemistry and Physics", 59th ed., 1978. [g] Theoretical heats of formation calculated from $E^{mol} - \Sigma E^A + \Sigma\Delta H_f{}^A$ where E^{mol} and E^A are the calculated total energies of the molecule and atoms, respectively. [h] The negative of the HOMO eigenvalue. [i] M. F. Guest, J. B. Pedley, and M. Horn, *J. Chem. Thermodyn.*, **1**, 345 (1969). [j] M. J. S. Dewar and M. L. McKee, in course of publication. [k] These experimental data were not included in ref 1 and are therefore excluded from the statistics here to preserve accurate comparability between data sets. [l] T. P. Fehlner, *Inorg. Chem.*, **14**, 934 (1975). [m] D. R. Lloyd, N. Lynaugh, P. J. Roberts, and M. F. Guest, *J. Chem. Soc., Faraday Trans 2*, 1382 (1975). [n] Unpublished calculations by W. Thiel. [o] This work.

Halgren et al.[1] all referred to experimental geometries while our own calculations included full geometry optimization at the MNDO level. Use of experimental geometries is incorrect in principle because if the experimental geometry for a molecule differs from the theoretical one, it will correspond to a completely arbitrary point on the calculated potential surface. Furthermore, since experimental geometries are subject to experimental error, there will be a corresponding uncertainty in the location of this point which may lead to a relatively large error in the corresponding energy, since the energy there is not stationary. This can be seen clearly from diagrammatic representation in Figure 1. It should also be noted that the errors introduced in this way by quite small differences in geometry are not negligible. Thus the MNDO energies for experimental geometries for the species listed in Table I are greater than the optimized ones by, on average, 2.1 kcal/mol and the individual differences show much scatter (0.2-8.5 kcal/mol). Since MNDO reproduces geometries as well as rather good ab initio methods,[3] it is likely that the other procedures[1] are subject to errors that are at least equally large.

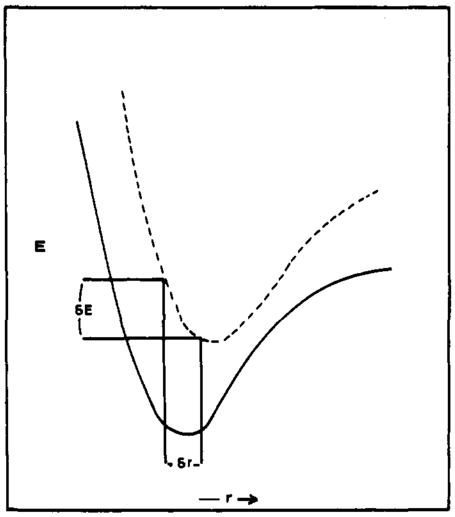
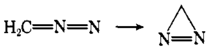
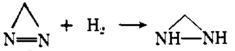
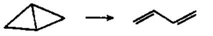
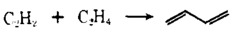


Figure 1. Schematic representation of the variation in energy of a molecule with changes in a coordinate r, actual (—) and calculated (. . .). The range (δr) of values of r, corresponding to possible experimental error in determining r, in turn corresponds to a relatively large change (δE) in calculated energy.

Ionization Potentials and Dipole Moments. Comparison of the MNDO ionization potentials (Koopmans' theorem) and dipole moments with the experimental data chosen by Halgren et al.[1] is made in Table I. Again, using the data tabulated by these authors[1] we have compiled the statistics in Table III. Apparently the overall agreement between the theoretical and experimental ionization potentials is about the same for PRDDO, STO-3G, MBS, and MNDO, while the extended basis set values are about twice as accurate and the CNDO/2

Table II. Comparison[a,b] of Calculated and Experimental Energies for 21 Formal Reaction Processes

process	ΔE, kcal mol^{-1} MNDO	ΔE, kcal mol^{-1} exptl
$B_2H_6 + B_4H_4 \rightarrow B_6H_{10}$	57.1	
$2B_2H_6 + B_5H_9 \rightarrow B_4H_{10} + B_5H_{11}$	−2.3	5.6
$B_4H_{10} + B_6H_{10} \rightarrow B_5H_9 + B_5H_{11}$	17.5	4.0
$B_5H_{11} + {}^3/_2B_2H_6 \rightarrow 2B_4H_{10}$	7.9	−5.7
$B_6H_{10} + B_{10}H_{14} \rightarrow 2B_8H_{12}$	16.9	
$B_8H_{12} + {}^1/_2B_2H_6 \rightarrow B_9H_{15}$	0.6	
$B_6H_{10} + B_9H_{15} \rightarrow B_5H_{11} + B_{10}H_{14}$	−12.8	
$B_6H_6{}^{2-} + B_{10}H_{14} \rightarrow B_6H_{10} + B_{10}H_{10}{}^{2-}$	−64.4	
$B_{10}H_{10}{}^{2-} + 2B_5H_{11} \rightarrow B_{10}H_{14}{}^{2-} + 2B_5H_9$	27.1	
$1,2\text{-}C_2B_4H_6 \rightarrow 1,6\text{-}C_2B_4H_6$	−3.5	
$2,4\text{-}C_2B_5H_7 + B_5H_9 \rightarrow 1,6\text{-}C_2B_4H_6 + B_6H_{10}$	12.6	
$2,4\text{-}C_2B_5H_7 + B_4H_{10} \rightarrow 4,5\text{-}C_2B_4H_8 + B_5H_9$	21.0	
$H_2 + C_2H_2 \rightarrow C_2H_4$	−42.7	−41.8
${}^3/_2C_2H_4 \rightarrow C_3H_6$	−11.8	−6.0
$H_2 + C_3H_4 \rightarrow C_3H_6$	−33.3	−33.1
$CH_3CN \rightarrow CH_3NC$	41.4	14.7
$2CH_3CN \rightarrow H_2C{=}N{=}N + C_3H_4$	73.1	75
	5.4	8
	−27.9	
	−35.1	−25.9
	−3.7	−41

[a] Calculated from the data in Table I. [b] These data extend the comparisons of Tables I and IX of ref 1.

ones four times worse. A similar but slightly less marked situation holds for dipole moments.

Time Required for Computation. In MINDO/3 and MNDO the determining factor is the time required for matrix diagonalization. Using procedures of the Householder type,[14] this varies approximately as the square of the number of basis set functions. We have found this relationship to hold over a very wide range of molecules, with up to 120 valence shell atomic orbitals.[15] Similar remarks apply to CNDO/2 and INDO where matrix diagonalization is again the time-determining step.

According to Halgren et al.,[1] PRDDO is 6 times, STO-3G 100 times, and the full MBS ab initio calculation 600 times slower than CNDO/2 (and therefore MNDO) for a system of 40 orbitals. Since the computation time for PRDDO depends on the cube, and STO-3G on the fourth power, of the number of basis functions, the ratios would be higher for larger systems.

In our laboratory MNDO calculations are always (as here) carried out with complete optimization of the geometry using an improved[16] version of the DFP[17] algorithm. The time required to carry out the geometry optimization increases approximately linearly with the number of variables to be optimized. The exact factor varies greatly since frequent one-dimensional line searches and restart procedures are carried out at points determined automatically by the program as the geometry optimization progresses. For the molecules calculated in ref 3b, using the experimental geometries as starting guesses, an average of 1.4 (standard deviation 0.7) SCF calculations per variable was required.[18]

Discussion

From the work of Halgren et al.[1] it is clear that, while several of the MO techniques currently in use (e.g., PRDDO, STO-3G, VRDDO, etc.) more or less closely approach the results of rigorous minimum basis set ab initio calculations, the latter are themselves in poor agreement with experiment, at least for calculated energies. Based on the data examined here the semiempirical MNDO method removes about 60% of the error in the MBS energy calculations while at the same time achieving comparable or slightly better accuracy in the prediction of ionization potentials and dipole moments. Indeed, the data chosen by Halgren et al. (and used here) form a particularly difficult test for MNDO since boron compounds are a class for which MNDO performs less well.[13] Moreover, the remaining compounds include several "difficult" cases. Thus of the 138 molecules containing C, H, N, and O examined in our original tests of MNDO the error in the heat of formation of methyl isocyanide was, with one exception, greater than that for any other molecule. Likewise, the MNDO dipole moments of methyl isocyanide and cyanide were the worst of 57 molecules for which comparison with experiment was possible. The errors incurred by MNDO are therefore in general[13] rather less than those listed in Table I.

Table III. Summary of Root Mean Square Errors for Seven MO Methods Relative to Experiment[a,b]

method	ΔE, kcal mol^{-1}	IP, eV	μ, D
CNDO/2	168.5 (11)	4.40 (14)	2.24 (10)
PRDDO	32.4 (11)	1.06 (14)	0.98 (10)
STO-3G	30.2 (11)	1.14 (14)	0.80 (7)
MBS	29.4 (11)	1.10 (14)	0.89 (10)
MBS	29.4 (11)	1.10 (14)	0.89 (10)
4-31G	14.0 (8)	0.57 (7)	0.41 (5)
double ζ	12.6[c] (8)	0.55 (10)	0.37 (5)
MNDO	10.8[d] (11)	1.01[d] (14)	0.83[d] (10)

[a] Calculated from the data in ref 1 except as noted. [b] The number of data pairs compared is given in parentheses. [c] This figure differs slightly from that derived from the data in Table IX of ref 1 where an incorrect value for the energy of the hydrogen molecule at the Snyder-Basch level was apparently employed. [d] Calculated from the data in Tables I and II.

The work of Halgren et al.[1] forms a very useful (and hitherto unavailable) comparison of the relative performance of the various MO methods for a number of specific molecules. While we in no way wish to belittle the efforts of these workers, we feel bound to point out that far more extensive testing is necessary to assess the value of a particular method as a practical tool. Although Halgren, Lipscomb, et al. assume that a similar pattern of success and failure is shared by the ab initio and semiempirical methods, regardless of the specific approximations involved, we believe that such an assumption must be justified by extensive testing. Only in this way, for example, have we been able to uncover certain systematic weaknesses in the MNDO procedure. These have been pointed out previously but are usefully reiterated here.[19] Thus four-membered ring compounds are predicted to be too stable and sterically crowded molecules too unstable while molecules containing NO bonds err in both directions.[3b] The stabilities of nonclassical ions are underestimated[3b] (a failing shared by MBS calculations[20]) and, presumably related to this, the activation energies for hydrogen-transfer reactions are overestimated[21] (a failing also shared by MBS calculations[22]). Single bond rotation barriers[3b] and the corresponding torsional vibration frequencies[23] are underestimated as is the puckering in cyclic compounds (MBS calculations also underestimate ring puckering[24]). One of the disappointing features of MNDO and one which we are urgently working to correct is its failure to give a proper account of hydrogen bonding (also shared by MINDO/3[25]). A number of authors[26] have attempted to use either the CNDO/2 or INDO schemes in this connection apparently unaware of the documented[27] failure of these methods to account correctly for nonbonded interactions. In particular nonbonded interactions which are expected to be highly repulsive are frequently predicted to be only weakly so, or even attractive. The fact that an attractive interaction is calculated for formally hydrogen bonded systems is therefore probably fortuitous. For example, an often-cited success of CNDO/2 theory is the predicted dimerization energy of water (5.9 kcal/mol, 8.4 with geometry optimization) which compares favorably with experimental (5.0 kcal/mol) and theoretical (4.7–12.6 kcal/mol) estimates.[28] However, Gregory and Paddon-Row[27b] have pointed out that CNDO/2 also predicts a similar stabilization energy (8.1 kcal/mol) for the OO bond dimer with an OO separation of 1.60 Å, while an INDO calculation suggested a stabilization of 24.2 kcal/mol with an OO distance of 1.45 Å. Repulsive energies of 203 and 101 kcal/mol were predicted by 4-31G[29] and MNDO, respectively, at an OO separation of 1.50 Å. Even more bizarre is the case of dimethyl sulfide, for which CNDO/2 predicts the SS dimer to be stabilized to the extent of 120 kcal mol^{-1} with an SS separation of 2.0 Å.[30,31] Numerous other examples of the failure of CNDO/2 to account properly for nonbonded interaction could be cited.[32]

In our view, one of the most serious problems associated with the use of larger basis set ab initio calculations is that their limits of error are uncertain. Many workers in this field in the past seem to have regarded the label "ab initio" as a guarantee of reliability and have consequently been little concerned with practical testing. Further uncertainty has been introduced by the use of inadequate procedures for calculating molecular geometries and by failure to characterize stationary points.[33] Happily, this situation is changing largely due to the efforts of the Pople group.[34]

Conclusions

Based on a limited set of test data suggested by Halgren, Lipscomb, and their co-workers, the MNDO method appears to be three times as accurate (relative to experimental data) as PRDDO, STO-3G, or MBS for relative energies and of comparable accuracy for ionization potentials and dipole moments. One SCF calculation using MNDO requires approximately the same computation time as CNDO/2. Complete geometry optimization of N_v variables requires, on average, ca. $1.5N_v$ SCF calculations.

Acknowledgments. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 79-0008) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out using the CDC 6400/6600 computed at the University of Texas Computation Center.

References and Notes

(1) T. A. Halgren, D. A. Kleier, J. H. Hall, Jr., L. D. Brown, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **100,** 6595 (1978).

(2) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97,** 1285, 1294, 1302, 1307 (1975).

(3) (a) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99,** 4989 (1977); (b) *ibid.*, **99,** 4907 (1977); (c) M. J. S. Dewar and M. L. McKee, *ibid.*, **99,** 5231 (1977); (d) M. J. S. Dewar and H. J. Rzepa, *ibid.*, **100,** 58 (1978).

(4) QCPE Newsletter 55, Department of Chemistry, Indiana University, Bloomington, Ind., 1976.

(5) It seems to us improper to claim for PRDDO a special status as a "semi-ab initio" method rather than a semiempirical one. A semiempirical treatment is by definition an ab initio one which has been modified by the introduction of adjustable parameters in place of calculated quantities. In the original paper, PRDDO was first introduced as an ab initio method,[6] but it has been subsequently used in a parametrized form, i.e., as a semiempirical one. NDDO also can be, and has been,[7] used as an ab initio procedure. MNDO is a corresponding semiempirical treatment. Although the results here seem to indicate that it is in fact more accurate than PRDDO, we see no reason to advertise the fact by trying to claim a new status for it.

(6) T. A. Halgren and W. N. Lipscomb, *J. Chem. Phys.*, **58,** 1569 (1973).

(7) J. Chandrasekhar, P. K. Mehrotra, S. Subramanian, and P. T. Manoharan, *Theor. Chim. Acta*, **41,** 243 (1976); R. D. Brown, F. R. Burden, and G. R. Williams, *ibid.*, **18,** 98 (1970); R. D. Brown, F. R. Burden, G. R. Williams, and L. F. Phillips, *ibid.*, **21,** 205 (1971).

(8) L. C. Snyder and H. Basch, "Molecular Wavefunction and Properties", Wiley, New York, 1972.

(9) Theoretical procedures lead to estimates of heats of atomization. For convenience in comparing them with experiment, we have converted them to heats of formation, using the experimental heats of formation of the gaseous atoms at 25 °C; see footnote *d*, Table I.

(10) Misleading claims frequently appear in print which imply much greater recovery of correlation energy. The fraction of the total correlation energy that can be recovered by, e.g., CI is in fact limited by the completeness of the basis set used. The higher figures refer to the percentage of *this* fraction that has been recovered, not that of the total correlation energy. With the largest basis sets in current use, the maximum possible recovery is ca. 80%.

(11) M. J. S. Dewar, *Science*, **187,** 1037 (1975).

(12) M. J. S. Dewar and M. L. McKee, *Inorg. Chem.*, **17,** 1569 (1978).

(13) Average absolute errors in the MNDO heats of formation (kcal/mol) were, for compounds containing CH, 6.0 (58 compounds); NO, 6.5 (80 compounds) B, 14.1 (45 compounds); F, 9.8 (71 compounds); total 8.7 (254 compounds).

(14) The remarks concerning computing times for MINDO/3 and MNDO are based on our routine use over several years of an assembly language version of the matrix diagonalization routine GIVENS (F. Prosser, QCPE No. 62, 1965). Recently we have found that on our system the FORTRAN routines from the EISPACK series of programs (B. T. Smith, J. M. Boyle, B. S. Garbow, Y. Ikebe, V. C. Klema, and C. B. Moler, "Eispack Guide". Lecture Notes in Computer Science, Vol. 6, Springer-Verlag, West Berlin, 1974; B. S. Garbow and J. J. Dongarra, "EISPACK Path Chart and Documentation for the EISPACK Package of Matrix Eigensystem Routines", Argonne National Laboratory, 1974) are of comparable efficiency. We are currently rewriting some of these routines in assembly language in the hope of further increasing their efficiency.

(15) Individual compounds show some scatter. In particular, the time required for those with high symmetry (e.g., C_2H_6, benzene) tends to be less than for less symmetrical analogues.

(16) P. K. Weiner, Ph.D. Dissertation, The University of Texas at Austin, 1975.

(17) R. Fletcher and M. J. D. Powell, *Comput. J.*, **6**, 163 (1963); W. C. Davidon, *ibid.*, **10,** 406 (1968).

(18) The choice of initial geometry is not important so long as it is in the right ball park. Initial convergence is very fast. Thus for a random sample of 36 molecules with up to 26 atoms, which we calculated in other connections with starting geometries estimated using "standard" bond lengths and angles, the number of SCF calculations per cycle was also ca. 1.5, the individual numbers lying in the range 0.5–3.0.

(19) In spite of the extensive tests that we have carried out, further systematic errors may remain. We would therefore be most grateful to hear of any such errors discovered in other laboratories.

(20) J. A. Pople, *Int. J. Mass Spectrom. Ion Phys.*, **19,** 89 (1976).

(21) S. B. Brown, M. J. S. Dewar, G. P. Ford, D. J. Nelson, and H. S. Rzepa, *J. Am. Chem. Soc.*, **100,** 7832 (1978).

(22) M. T. Rayez-Meaume, J. J. Dannenberg, and J. L. Whitten, *J. Am. Chem. Soc.*, **100,** 747 (1978).

(23) For several examples, see: M. J. S. Dewar, G. P. Ford, M. L. McKee, W. Thiel, H. S. Rzepa, and Y. Yamaguchi, *J. Mol. Struct.*, **43,** 135 (1978).

(24) D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, **97,** 1354 (1975).

(25) T. J. Zielinski, D. L. Breen, and R. Rein, *J. Am. Chem. Soc.*, **100,** 6266 (1978); G. Klopman, P. Andreozzi, A. J. Hopfinger, O. Kikuchi, and M. J. S. Dewar, *ibid.*, **100,** 6267 (1978).

(26) For recent references see, for example, J. Catalán, M. Yáñez, and J. I. Fernández-Alonzo, *J. Am. Chem. Soc.*, **100,** 6917 (1978).

(27) (a) A. R. Gregory and M. Przybylska, *J. Am. Chem. Soc.*, **100,** 943 (1978); (b) A. R. Gregory and M. N. Paddon-Row, *ibid.*, **98,** 7521 (1976); (c) A. R. Gregory, *Jerusalem Symp. Quantum Chem. Biochem.*, **6**, 23 (1974).

(28) P. A. Kollman and L. C. Allen, *Chem. Rev.*, 7**2,** 283 (1972), and references cited therein.

(29) L. Carlsen and J. P. Snyder, *J. Org. Chem.*, **43,** 2216 (1978); see also W. Thiel, *Theor. Chim. Acta*, **48,** 357 (1978).

(30) D. B. Boyd, *J. Phys. Chem.*, **82,** 1407 (1978).

(31) The MNDO method predicts this interaction to be repulsive at all distances. However, a MINDO/3 calculation predicted a small (6 kcal/mol) stabilization at an SS distance of 2.49 Å.[30] It now appears that there are problems associated with the use of MINDO/3 for the third-period elements Si, P, and S; see note added by M. J. S. Dewar and G. P. Ford in G. Frenking, H. Goetz, and F. Marschner, *J. Am. Chem. Soc.*, **100,** 5295 (1978).

(32) A. R. Gregory, Ph.D. Thesis, The Australian National University, 1972, and references cited therein. For a very recent example, see: K. B. Lipkowitz, *J. Am. Chem. Soc.*, **100,** 7535 (1978).

(33) As our work has clearly shown,[23] it is very easy to mistake for minima stationary points which in fact are saddle points and for saddle points (i.e., transition states) points which are maxima in more than one independent geometrical coordinate. For reliable predictions to be made of chemical behavior, it is essential that stationary points be characterized by calculating and diagonalizing the corresponding Hessian (force constant) matrices; see J. W. McIver, Jr., and A. Komornicki, *J. Am. Chem. Soc.*, **94,** 2625 (1972); J. W. McIver, *Acc. Chem. Res.*, 7, 72 (1974). The calculation of second derivatives is quite feasible in MNDO for much larger molecules than in even an MBS treatment.

(34) See, for example, W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11,** 175 (1974).