(IV) Conclusions

It is evident from the above results that the use of population optimized basis functions can result in a method which, compared to the methods presently used for one-center integrals in most semiempirical methods, requires fewer parameters but predicts with equal or better accuracy the energies of atoms and ions in a wide variety of states. The absence of parameters which depend on atom type may open the path to a semiempirical molecular orbital method which will be relatively easy to parameterize for a wide variety of atoms.

The accuracy of the atomic energy predictions will probably be improved by development of a modified form of eq 1 involving spin populations. Such a form should be used in open shell molecular orbital calculations and, of course, in the above calculations of valence shell atomic energies, as few of the states calculated were closed shell. The improvement such a modification would make, however, must be no larger than the relatively small error in the present calculations.

An additional path for improvement is the inclusion of external coulombic effects on the orbital optimization. This additional effect may well be necessary in future molecular calculations using population optimized basis functions.

Acknowledgment. We wish to thank the Georgetown University Central Computer Facility for providing access to the IBM 370/145 on which this work was done.

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Ground States of Molecules. 38.[1] The MNDO Method. Approximations and Parameters

Michael J. S. Dewar* and Walter Thiel

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712.

Received October 27, 1976

Abstract: The basic approximations of the MNDO (modified neglect of diatomic overlap) method are described including a semiempirical model for the two-center repulsion integrals. Parametric functions for the various terms in the MNDO Fock matrix are then chosen which contain atomic parameters only (no bond parameters). Using a nonlinear least-squares iterative optimization technique, numerical values of the parameters are determined for the elements H, C, N, O. Finally, the main differences between the MNDO and MINDO methods are discussed.

(I) Introduction

The primary objective of the work reported in this series of papers has been the development of a quantitative treatment of molecular properties accurate enough, reliable enough, and cheap enough to be of practical value in chemistry, in particular in areas where experimental data are lacking or where current experimental procedures fail. For reasons that have been discussed in detail elsewhere,[2] we have always felt that the only hope of success lay in a parametric approach and our efforts have accordingly been directed to such semiempirical versions of the Roothaan[3]-Hall[4] (RH) SCF-LCAO-MO method.

In order to keep the cost of the calculations within bounds, it is necessary to simplify the RH treatment. Our previous work has been based on the simplified versions developed by Pople et al.,[5] in particular INDO.[6] Here the number of electron repulsion integrals is greatly reduced by using the core approximation, together with a minimum basis set of valence shell AO's, and by neglecting all integrals involving differential overlap except for the one-electron core resonance integrals ($\beta_{\mu\nu}$) and one-center exchange integrals ($\mu\nu$, $\mu\nu$).

The core approximation is certainly reasonable and the neglect of electron repulsion integrals involving diatomic differential overlap can also be justified.[7] These are the assumptions made in the NDDO approximation.[6,8] The further neglect of electron repulsion integrals involving one-center overlap, as in INDO, is, however, unjustifiable,[7] so NDDO would seem the logical basis for a semiempirical treatment. In previous studies we have nevertheless used INDO because the problems of parametrization are much simpler and because less computation is involved.

In the CNDO[5,9] and INDO[5,6] approximations, the repulsion integrals ($\mu\mu$, $\nu\nu$) between any AO ϕ_μ of atom A and any AO ϕ_ν of atom B are set equal ($=\gamma_{AB}$), regardless of whether ϕ_μ and ϕ_ν are of s, pσ, or pπ type. This simplification is essential if the results of the calculation are to be invariant for rotation of the coordinate axes.[5,8] The integrals are not in fact equal and in NDDO they are not assumed to be equal. Moreover in NDDO there are a number of additional bicentric integrals to be considered, which involve one-center differential overlap and are consequently neglected in CNDO or INDO. For a given pair of dissimilar first-row atoms, there are 22 distinct bicentric NDDO integrals to be determined instead of just one in the simple treatments.

In the NDDO calculations so far reported (e.g., ref 10–13) the electron repulsion integrals were found by direct quadrature, using Slater–Zener orbitals. Such an approach runs counter to the philosophy[2] underlying treatments of the MINDO type where allowance is made for electron correlation by suitable modification of the electron repulsion integrals. In our INDO-based treatments,[14-16] which we term MINDO, there is just one such integral to be determined for each pair of atoms. The problem is therefore similar to that involved in the analogous treatment of conjugated molecules, using the Hückel σ, π approximation, and can be solved in a similar manner, using the approach suggested by Pariser and Parr.[17] The problem in NDDO is much more difficult since there are now 22 distinct bicentric integrals to be evaluated. It is not at all obvious how schemes appropriate to the π approximation or MINDO can best be generalized to meet the requirements of NDDO.

One such formalism was developed here 2 years ago and used in a preliminary parametrization[18] of NDDO. While the resulting treatment[19] seemed promising and certainly succeeded in overcoming certain difficulties that had been encountered in MINDO, the underlying formalism suffered from certain inconsistencies. We have now developed[20] an alternative and seemingly more attractive procedure for estimating the NDDO repulsion integrals and have used it in a complete reparametrization of NDDO for hydrogen, carbon, nitrogen, and oxygen. This paper describes the development of the new treatment, which we term MNDO,[19] together with the final values for the parameters. The following papers compare results for various properties of a wide range of molecules calculated by MNDO with those given by the final version of MINDO (MINDO/3[16]) and by experiment.

(II) Basic Approximations

The treatment here is confined to closed shell molecules and to the valence electrons in them, these being assumed to move in the field of a fixed core composed of the nuclei and inner shell electrons (core approximation). The valence shell MO's (ψ_i) are represented by linear combinations of a minimum basis set of valence shell AO's (ϕ_ν);

$$\psi_i = \sum_\nu C_{\nu i}\phi_\nu \qquad (1)$$

The coefficients $C_{\nu i}$ are found from the Roothaan[3]-Hall[4] equations which in the NDDO approximation assume the form:

$$\sum_\nu (F_{\mu\nu} - E_i\delta_{\mu\nu})C_{\nu i} = 0 \qquad (2)$$

where E_i is the eigenvalue of the MO ψ_i and $\delta_{\mu\nu}$ the Kronecker δ. The elements $F_{\mu\nu}$ of the Fock matrix are the sum of a one-electron part $H_{\mu\nu}$ (core Hamiltonian) and a two-electron part $G_{\mu\nu}$, and the electronic energy E_{el} is given by:

$$E_{\text{el}} = \tfrac{1}{2}\sum_\mu\sum_\nu P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) \qquad (3)$$

where $P_{\mu\nu}$ is an element of the bond order matrix.

From now on, we shall assume that the AO's ϕ_μ and ϕ_ν are centered at atom A and the AO's ϕ_λ and ϕ_σ at atom B (A $\neq$ B). If necessary, superscripts A or B will assign a particular symbol to atom A or B, respectively. In this notation, the NDDO Fock matrix elements are:

$$F_{\mu\mu} = U_{\mu\mu} + \sum_{\text{B}} V_{\mu\mu,\text{B}} + \sum_{\nu}^{\text{A}} P_{\nu\nu}[(\mu\mu,\nu\nu) - \tfrac{1}{2}(\mu\nu,\mu\nu)] + \sum_{\text{B}}\sum_{\lambda,\sigma}^{\text{B}} P_{\lambda\sigma}(\mu\mu,\lambda\sigma) \qquad (4)$$

$$F_{\mu\nu} = \sum_{\text{B}} V_{\mu\nu,\text{B}} + \tfrac{1}{2} P_{\mu\nu}[3(\mu\nu,\mu\nu) - (\mu\mu,\nu\nu)] + \sum_{\text{B}}\sum_{\lambda,\sigma}^{\text{B}} P_{\lambda\sigma}(\mu\nu,\lambda\sigma) \qquad (5)$$

$$F_{\mu\lambda} = \beta_{\mu\lambda} - \tfrac{1}{2}\sum_{\nu}^{\text{A}}\sum_{\sigma}^{\text{B}} P_{\nu\sigma}(\mu\nu,\lambda\sigma) \qquad (6)$$

The following terms appear in the Fock matrix:

(a) One-center one-electron energies $U_{\mu\mu}$ which represent the sum of the kinetic energy of an electron in AO ϕ_μ at atom A and its potential energy due to the attraction by the core of atom A.

(b) One-center two-electron repulsion integrals, i.e., Coulomb integrals $(\mu\mu, \nu\nu) = g_{\mu\nu}$ and exchange integrals $(\mu\nu, \mu\nu) = h_{\mu\nu}$.

(c) Two-center one-electron core resonance integrals $\beta_{\mu\lambda}$.

(d) Two-center one-electron attractions $V_{\mu\nu,\text{B}}$ between an electron in the distribution $\psi_\mu\psi_\nu$ at atom A and the core of atom B.

(e) Two-center two-electron repulsion integrals $(\mu\nu, \lambda\sigma)$.

The total energy $E_{\text{tot}}^{\text{mol}}$ of the molecule is the sum of the electronic energy E_{el} and the repulsions $E_{\text{AB}}^{\text{core}}$ between the cores of atoms A and B.

$$E_{\text{tot}}^{\text{mol}} = E_{\text{el}} + \sum_{\text{A}<\text{B}}\sum E_{\text{AB}}^{\text{core}} \qquad (7)$$

The heat of formation ΔH_f^{mol} of the molecule is obtained from its total energy by subtracting the electronic energies E_{el}^{A} and adding the experimental heats of formation ΔH_f^{A} of the atoms in the molecule;[21]

$$\Delta H_f^{\text{mol}} = E_{\text{tot}}^{\text{mol}} - \sum_{\text{A}} E_{\text{el}}^{\text{A}} + \sum_{\text{A}} \Delta H_f^{\text{A}} \qquad (8)$$

The electronic energies of the atoms are calculated from restricted single-determinantal wave functions using the same approximations and parameters as in molecular NDDO calculations.

In our approach, the various terms in the Fock matrix and the repulsions $E_{\text{AB}}^{\text{core}}$ are not evaluated analytically. They are determined either from experimental data or from semiempirical expressions which contain numerical parameters that can be adjusted to fit experimental data. It is hoped that the introduction of adjustable parameters will compensate both for the basic deficiencies of the single-determinantal MO approach (i.e., neglect of electronic correlation) and for the additional errors due to the simplifying assumptions of the NDDO scheme.

We shall now discuss the semiempirical approximations that we considered for the various quantities in the NDDO treatment. Our choices were partly guided by previous experiences with the MINDO parametrization.

The one-center terms $U_{\mu\mu}$, $g_{\mu\nu}$, and $h_{\mu\nu}$ appear in the INDO and NDDO Fock matrix and can be treated similarly in both cases. In MNDO, these terms are evaluated as in MINDO/3,[16] using a procedure[22] based on Oleari's method,[23] in which the theoretical energies of several valence states of the atom and its ions are fitted to the corresponding spectroscopic values. Since this procedure[22] allows an independent calculation of all the one-center terms, it is preferable to the alternatives based on the Slater–Condon parameters[6] (e.g., INDO,[6] MINDO/1,[14] and MINDO/2,[15]) where certain relationships between the one-center integrals have to be assumed.

The semiempirical values[22] for the one-center repulsion integrals $g_{\mu\nu}$ and $h_{\mu\nu}$ are much smaller than the corresponding analytical values. This reduction is attributed[17] to the Coulombic correlation between the motions of the electrons which tends to keep them apart at every moment and to decrease their repulsion. By deriving the one-center repulsion integrals from experimental data, we automatically make some allowance for the correlation effects that are formally neglected in the MO approach.

In this situation, it would clearly be inconsistent to evaluate the two-center repulsion integrals from analytical formulas,

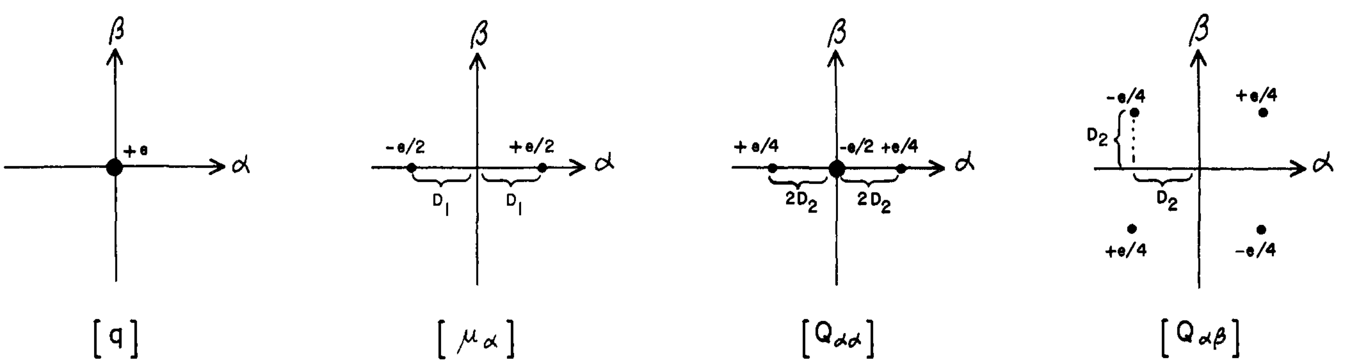

Figure 1. Point charge configurations corresponding to various multipoles.

as was done in the published NDDO studies.[10-13] We have therefore developed a semiempirical model for these integrals that takes correlation effects into account. We shall now describe the basic approximations of the model, mathematical details being given elsewhere.[20]

The two-center repulsion integrals $(\mu\nu, \lambda\sigma)$ represent the energy of interaction between the charge distributions $e\phi_\mu\phi_\nu$ at atom A and $e\phi_\lambda\phi_\sigma$ at atom B (elementary charge e). Classically, they are equal to the sum over all interactions between the multipole moments M_{lm} of the two charge distributions,[24] the subscripts l and m specifying the order and orientation of the multipoles. Based on this classical concept, the two-center repulsion integrals are expanded[25,26] in terms of semiempirical multipole-multipole interactions $[M^A_{l_1m}, M^B_{l_2m}]$:

$$(\mu\nu, \lambda\sigma) = \sum_{l_1}\sum_{l_2}\sum_{m} [M^A_{l_1m}, M^B_{l_2m}] \tag{9}$$

The semiempirical multipole-multipole interactions are required to show the correct behavior in the limits $R_{AB} \to \infty$ and $R_{AB} \to 0$ (interatomic distance R_{AB}). For $R_{AB} \to \infty$, they have to converge to the classical values for the interactions. For $R_{AB} = 0$, they must reproduce the semiempirical values for the corresponding one-center repulsion integrals (see above). Both requirements are met by the following point charge approximation:

Each multipole M_{lm} is represented by an appropriate configuration $[M_{lm}]$ of 2^l point charges of magnitude $e/2^l$, with charge separations D_l. The interaction $[M^A_{l_1m}, M^B_{l_2m}]$ between two multipoles is then calculated by applying an appropriate semiempirical formula to each of the interactions between the point charges in the two configurations and by summing over all these point charge interactions. Denoting the distance between the point charges i and j in the interacting configurations at atoms A and B by R_{ij}, we obtain:

$$[M^A_{l_1m}, M^B_{l_2m}] = \frac{e^2}{2^{l_1+l_2}} \sum_{i=1}^{2^{l_1}} \sum_{j=1}^{2^{l_2}} f_1(R_{ij}) \tag{10}$$

where $f_1(R_{ij})$ stands for any semiempirical expression which behaves properly in the limits $R_{AB} \to \infty$ and $R_{AB} \to 0$.

In order to calculate the distances R_{ij} for a given interatomic distance R_{AB}, we have to define the relevant point charge configurations. With a minimal sp basis set for the valence electrons, there are only four configurations to be considered which are shown in Figure 1. [q] represents the monopole of the charge distributions ss and $p_\alpha p_\alpha$, $[\mu_\alpha]$ the dipole of the distributions sp_α, $[Q_{\alpha\alpha}]$ the linear quadrupole of the distributions $p_\alpha p_\alpha$, and $[Q_{\alpha\beta}]$ the square quadrupole of the distributions $p_\alpha p_\beta$ ($\alpha,\beta = x, y,$ or z). No other configurations are necessary since the higher multipole moments of our charge distributions vanish by symmetry.

The charge separations D_l in the dipole and quadrupole configurations (see Figure 1) are determined by the condition that the multipole moment of each configuration is equal to that of the corresponding charge distribution. For first-row atoms, we obtain:[20]

$$D_1 = \frac{5}{3^{1/2}} \frac{(4\zeta_{2s}\zeta_{2p})^{5/2}}{(\zeta_{2s} + \zeta_{2p})^6} \tag{11}$$

$$D_2 = (3/2)^{1/2} \zeta_{2p}^{-1} \tag{12}$$

where ζ_{2s} and ζ_{2p} are the Slater exponents of the 2s and 2p AO, respectively. The values used are shown in Table IV (see eq 25).

For the semiempirical function $f_1(R_{ij})$ in (10), we investigated the use of formulas based on the Dewar-Sabelli[27]-Klopman[28] (DSK) approximation:

$$f_1(R_{ij}) = [R_{ij}^2 + (\rho^A_{l_1} + \rho^B_{l_2})^2]^{-1/2} \tag{13}$$

and on the Mataga-Nishimoto[29] (MN) approximation

$$f_1(R_{ij}) = \left[R_{ij} + \frac{1}{\rho^A_{l_1} + \rho^B_{l_2}} \right]^{-1} \tag{14}$$

With an sp basis set, both functions make use of three additive terms ρ_l for each element which are characteristic of monopole, dipole, and quadrupole ($l = 0, 1, 2$). The additive terms ρ_l are chosen so that eq 10 yields the correct semiempirical one-center limit for the interaction between two monopoles (g_{ss}), two dipoles (h_{sp}), and two quadrupoles (h_{pp}). Accordingly, ρ_0 is equal to $e^2/2g_{ss}$ in the DSK approximation and to $g_{ss}/2e^2$ in the MN approximation; the values for ρ_1 and ρ_2 are calculated by numerical methods.[20]

Having defined the charge separations D_l and the additive terms ρ_l, the semiempirical expressions for the two-center MNDO repulsion integrals are given by (9), (10), (13), and (14). The integral (ss, sp_z) will serve as an example.

For (ss, sp_z), expansion 9 reduces to a single term, $[q^A, \mu^B_z]$, since all other multipole moments vanish. With the local coordinate system shown in Figure 2, we obtain by inspection, in the DSK approximation:

$$\begin{aligned}(\mathrm{ss}, \mathrm{sp}_z) = [q^A, \mu^B_z] = &-(e^2/2)[(R_{AB} - D^B_1)^2 \\ &+ (\rho^A_0 + \rho^B_1)^2]^{-1/2} \\ &+ (e^2/2)[(R_{AB} + D^B_1)^2 + (\rho^A_0 + \rho^B_1)^2]^{-1/2}\end{aligned} \tag{15}$$

Analogous explicit formulas for all the nonvanishing two-center repulsion integrals are available[20] for the local coordinate system of Figure 2. In MNDO, the semiempirical integrals are first calculated from these formulas in the local coordinate system and then transformed to the molecular coordinate system.

It should be noted that our definitions of the charge separations D_l and the additive terms ρ_l ensure the proper behavior of each semiempirical repulsion integral in the limits $R_{AB} \to \infty$ and $R_{AB} \to 0$. Comparison of the semiempirical and analytical integrals shows[20] that both are very similar at large interatomic distances ($R_{AB} > 3$Å); at small and medium distances, the semiempirical integrals are appreciably smaller,

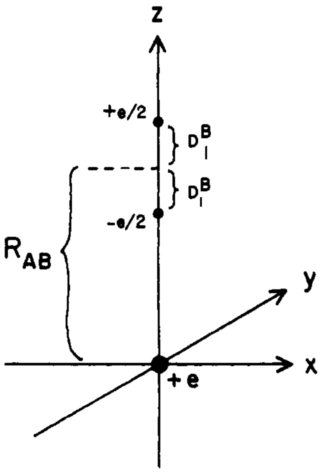

Figure 2. Two interacting point charge configurations [q^A, $\mu_z{}^B$]. The nucleus of atom A is in the origin of the coordinate system, and that of atom B on the positive z axis at a distance R_{AB}.

the difference increasing with increasing overlap of the two interacting charge distributions, due to the inclusion of correlation effects in the semiempirical integrals.

Let us now turn to the core-electron attractions $V_{\mu\nu,B}$ and the core-core repulsions $E_{AB}{}^{core}$. In semiempirical methods, these quantities are usually expressed in terms of the two-center repulsion integrals, for the following reasons. Early work at the CNDO and INDO level indicated[6,9] that the core-electron attractions are best represented by a Goeppert-Mayer-Sklar potential with neglect of penetration integrals, in order to avoid a collapse of molecular geometries to extremely short bond lengths. The neglect of the penetration integrals decreases the absolute values of the core-electron attractions significantly; as a consequence, the core-core repulsions must likewise be reduced from their point-charge values $Z_AZ_Be^2/R_{AB}$ (core charges Z_A and Z_B) in order to keep the balance between the attractions and repulsions in the molecule.

In the development of the MNDO method, we investigated the following functions for the core-electron attractions and the core-core repulsions:

$$V_{\mu\nu,B} = -Z_B(\mu^A\nu^A, s^Bs^B) + f_2(R_{AB}) \tag{16}$$

$$E_{AB}{}^{core} = Z_AZ_B(s^As^A, s^Bs^B) + f_3(R_{AB}) \tag{17}$$

Note that in (16) and (17) the effect of the atomic core is simulated by the valence-shell charge distribution ss which, like the core, has no multipole moments higher than the monopole.

If the functions $f_2(R_{AB})$ in (16) and $f_3(R_{AB})$ in (17) are both zero, the net electrostatic interaction between two neutral atoms almost vanishes for every value of R_{AB} since the two-center two-electron repulsions, the core-electron attractions, and the core-core repulsions almost cancel.[30] This would be quite unrealistic since we expect the net electrostatic repulsion between neutral atoms to increase slowly with decreasing interatomic distance. This effect can be reproduced by proper choice of the functions $f_2(R_{AB})$ and $f_3(R_{AB})$. In our studies, we always assumed one of the two functions to be zero and tried different expressions for the other function. These expressions usually included an exponential term of the form $\exp(-\alpha R_{AB})$, with an adjustable α parameter, so that the net repulsion between neutral atoms vanishes in the limit $R_{AB} \rightarrow \infty$.

The remaining quantities in the MNDO method are the one-electron resonance integrals $\beta_{\mu\lambda}$ which provide the main contribution to the bonding energy of a molecule.[31] As in most previous semiempirical methods,[5,14-16] they are assumed to be proportional to the corresponding overlap integrals $S_{\mu\lambda}$:

$$\beta_{\mu\lambda} = f_4(R_{AB})S_{\mu\lambda} \tag{18}$$

The overlap integrals between the Slater basis AO's are evaluated analytically, the orbital exponents being treated as adjustable parameters (Table III). For the functions $f_4(R_{AB})$ in (18), we did not study any expressions with an explicit dependence on the interatomic distance R_{AB} although it is in principle possible to include such a dependence. The expressions we investigated always contained an adjustable β parameter in $f_4(R_{AB})$.

(III) Parametrization Procedure

Our next problem is to determine the best forms for the parametric functions f_1-f_4 and the best values of the parameters in them. We have been unable to find any theoretical considerations that are of the slightest assistance in this connection. The parameters in treatments such as this are so intimately interlinked that it is impossible to predict the effects of changes in them or, conversely, to deduce the changes that should be made in order to correct some specific error. The only feasible procedure is a purely empirical one, based on comparisons of calculated and observed properties for a carefully chosen "basis set" of molecules. The main factors to be considered are the ability of a given set of functions and parameters to reproduce the whole range of properties being studied and the uniformity of the errors over the compounds in the basis set. The latter should of course be chosen to cover as many different types of bonding situations as possible. The final candidate is then tested by calculations for a wide range of molecules, concentrating on those which previous experience has shown to be the most recalcitrant. If the results for some particular type of molecule are unsatisfactory, e.g., compounds containing triple bonds or four-membered rings, the parametrization is repeated using a basis set in which additional compounds of this type are included.

For a given choice of functions f_1-f_4, the parameters are determined by a nonlinear least-squares optimization procedure recently developed here,[32] based on an algorithm devised by Bartels.[33] Our problem is to find the optimum values for a set of parameters X_k ($k = 1, 2, \ldots, K$) by fitting the measured values Y_l ($l = 1, 2, \ldots, L$) of L properties of the M molecules in the basis set. This is done by minimizing the sum (Y) of the squares of the weighted errors ΔY_l in the calculated values;

$$Y = \sum_{l=1}^{L} (\Delta Y_l)^2 = \sum_{l=1}^{L} [Y_l(\text{calcd}) - Y_l(\text{obsd})]^2 W_l{}^2 \tag{19}$$

where W_l is a weighting factor for the quantity Y_l. Choice of the weighting factors allows different emphasis to be given to errors in different types of property (total energy, bond lengths, bond angles, dipole moments, ionization potentials, etc.).

We need to find the minimum of Y as a function of the parameters X_k, i.e., a minimum in a K-dimensional surface. The most efficient methods for solving such problems are based on an iterative procedure. Starting at a point defined by a given set of values for the parameters X_k, we estimate the best direction in which to proceed to reach the minimum. A line search in this direction leads to a first approximation to the minimum, and the procedure is then repeated using this as the starting point.

The simplest treatment of this kind is the method of steepest descents, where the search direction vector is taken to be the direction of maximum gradient. More sophisticated procedures (e.g., Davidon-Fletcher-Powell,[34] Murtagh-Sargent[35]) determine the search direction vector using an approximation to the inverse Hessian matrix which is updated in each cycle. All these procedures, however, need values for the derivatives of the function being minimized with respect to all the variables. In the present case, derivatives of Y with respect to the parameters X_k can be found only by finite difference which in-

Table I. Standard Molecules and Reference Functions for Parametrization with Fixed Geometries

Molecule	Reference functions			
	ΔH_f[a]	Grad[b]	IP[c]	μ[d]
H_2	X	X	X	
CH_4	X	X	X	
C_2H_6	X	X		
C_2H_4	X	X	X	
C_2H_2	X	X	X	
	X			
	X	X		
	X		X	
$C(CH_3)_4$	X			
N_2	X	X	X	
NH_3	X	X	X	X
CH_3NH_2	X	X		X
$(CH_3)_2NH$	X			X
NH	X			
N_2H_4	X	X		
HCN	X	X	X	X
CH_3CN	X	X		
$(CN)_2$	X			
H_2O	X	X	X	X
CH_3OH	X	X	X	X
$(CH_3)_2O$	X	X	X	X
O	X			
H_2O_2	X	X		
O_3	X			
CO	X	X	X	X
CO_2	X	X	X	
H_2CO	X	X	X	X
$(CH_3)_2CO$	X			
CH_2CO	X	X		
$(CHO)_2$	X			
HCOOH	X			X
$HCOOCH_3$	X			

[a] Heat of formation. [b] Gradient of the energy with respect to a geometrical variable. Note that for each of the molecules marked, the gradients for *all* independent geometrical variables are included as reference functions; e.g., for ethylene, the list of reference functions contains three gradients (C–C bond length, C–H bond length, HCC angle). [c] First ionization potential. [d] Dipole moment.

volves a large number of SCF calculations (more SCF calculations, in fact, than to carry out the actual line search). The amount of computation required would become excessive even for molecules of moderate size.

We therefore decided to use Bartels' nonlinear least-squares procedure[33] which assumes an initial search direction and refines this by information generated in the successive line searches, without calculating derivatives. The number of function evaluations (in our case SCF calculations) is thereby greatly reduced. The main difficulty lies in the arbitrary choice of the initial search direction. To account for the possibility that this is not realistic, each fourth cycle is used to explore a direction orthogonal to the predicted one ("side step") which ensures that no parts of the surface are overlooked. The parameterization procedure based on Bartels' algorithm is clearly superior to the one[15] previously used here for four reasons. First, it does not rely on the validity of first-order Taylor expansions. Second, it adjusts all parameters simultaneously. Third, it does not suffer from nonconvergence. And fourth, it is completely automatic once the following information has been provided: (a) set of M standard molecules, L reference quantities Y_l, and weighting factors W_l, (b) starting values for the K parameters X_k to be optimized; (c) convergence criteria for the optimization.

Table II. Weighting Factors

Reference function	Weighting factor[a]
Heat of formation	1 $kcal^{-1}$ mol
Ionization potential	10 eV^{-1}
Dipole moment	20 D^{-1}
Gradient for bond length[b]	4×10^{-6} $kcal^{-1}$ mol Å
Gradient for bond angle[b]	8×10^{-4} $kcal^{-1}$ mol deg
Gradient for dihedral angle[b]	2×10^{-3} $kcal^{-1}$ mol deg
Bond length[c]	100 $Å^{-1}$
Bond angle[c]	(2/3) deg^{-1}
Dihedral angle[c]	(1/3) deg^{-1}

[a] The dimensions are chosen to make the weighted errors ΔY_l dimensionless. [b] For parametrization with fixed geometries. [c] For parametrization with optimized geometries.

The reference functions for our standard molecules (see Table I) include heats of formation, geometrical variables, dipole moments, and first vertical ionization potentials, the latter being calculated by Koopmans' theorem.[36] As regards geometrical variables, two procedures are possible. In the first ("fixed geometries") the calculations are carried out at the experimental geometries, and the gradients of the energy with respect to the geometrical variables are taken as reference functions. In the second ("optimized geometries"), the geometries are calculated by minimizing the energy by the DFP method,[34] the optimized bond lengths, bond angles, and dihedral angles being directly used as reference quantities. Calculations with fixed geometries are at least ten times faster than those with optimized geometries and the results are not greatly different. We therefore used fixed geometries in preliminary studies of the performance of different parametric functions (f_1–f_4). The final parametrizations were of course carried out using optimized geometries.

In the parametrization for the elements C, H, N, and O, we divided the reference compounds into three groups, namely hydrocarbons, CHN systems, and CHO systems. Each group contained about ten standard molecules and was parametrized separately. The parameters for C and H were first determined from the first (hydrocarbon) group; these were then taken as constants in the parametrizations for N and O from compounds of the two other groups.

Table I contains the standard molecules and reference quantities used in the first stage of the parameterization (fixed geometries). Note that we do in effect parametrize for geometries at this stage since we minimize, inter alia, the gradients of the energy with respect to the geometrical variables. Thereby we adjust the parameters to reproduce equilibrium structures without optimizing the molecular geometries.

In the second stage of the parameterization (optimized geometries), each of the three groups was at first still treated separately. The standard molecules and reference quantities were essentially the same as in the first stage, with the obvious exception that the gradients were replaced by the corresponding variables in the list of reference quantities.[37] The parameters were then refined by a final parametrization including the molecules from all three groups, with the heats of formation as the only reference functions, and with simultaneous adjustment of all the parameters.

The weighting factors W_l for the various reference quantities are listed in Table II. With the selected sets of reference quantities (see Table I), the values chosen for the weighting factors ensure that the errors in the heats of formation usually amount to more than half of the total error (typically about

60%) and that most of the remaining error usually comes from the geometrical variables.

The initial guess for the parameters was found to be quite important. Often there are several different sets of parameters that correspond to local minima of the function Y. Depending on our initial guess, the optimization may converge to an unfavorable local minimum with a high final Y value. Also, if we begin our search far away from any minimum, the optimization may initially lead to some unreasonable region of the surface from which it is hard to escape later; this is probably due to the approximate nature of the search direction vector at the beginning of the optimization.

Since we encountered these difficulties on several occasions, we tried to find good initial guesses by a grid-type search in which each of the parameters was varied in steps over a physically reasonable range. This procedure provided some information about the general shape of the surface in the region of interest. For each combination of parametric functions investigated, we used this information to select at least three different initial sets of parameters. These sets were then optimized separately, and the results were considered to be reliable only if the separate optimizations converged to the same minimum.

Our program terminates if the value of Y can no longer be lowered by adjusting the parameters. Near the end of the optimization, there are usually a large number of cycles for which the value of Y is decreased by a very small amount in each cycle. Sometimes, however, such periods are followed by sudden further reductions in Y, probably because the search direction vector has been updated efficiently during these periods, as a result of information derived from "side steps" (see above). We therefore adopted the rule that we terminate an ongoing optimization only if "side steps" have been taken in all possible search directions and if subsequently there have been at least 20 cycles without much progress. Thus for K parameters, we optimize at least for $4K + 20$ cycles.[38,39]

The standardized procedure described above was used in all our parametrization studies. This enabled us to compare the performances of different parametric functions reliably. The choices for the sets of standard molecules and reference functions are certainly arbitrary, and different choices would probably lead to slightly different parameters. The selected sets, however, seem to be representative in the sense that the parameters obtained yield reasonable results for the molecules not included in the parametrization; this was often not true for smaller sets which we had tested initially.

(IV) Choice of Parametric Functions

Within the framework of the basic MNDO approximations, we have determined hydrocarbon parameters for about ten different combinations of parametric functions. We also parametrized the CHN and CHO systems using the five most promising sets of functions. Several conclusions follow from these studies.

With regard to the one-center terms $U_{\mu\mu}$, $g_{\mu\nu}$, and $h_{\mu\nu}$, we had to decide whether to keep them constant at Oleari's values[22,23] or to treat them as adjustable parameters. The one-center terms are found to have little influence on the calculated heats of formation and geometries. Dipole moments and ionization potentials, however, strongly depend on the values of the $U_{\mu\mu}$ parameters. We therefore decided to treat the $U_{\mu\mu}$ terms as variable parameters but to retain Oleari's values[22,23] for the one-center repulsion integrals $g_{\mu\nu}$ and $h_{\mu\nu}$.[40] This procedure was also used in MINDO/3.[16]

In the case of the two-center repulsion integrals, we can choose between the DSK approximation, eq 13, or the MN approximation, eq 14, for the point charge interaction $f_1(R_{ij})$. The two-center repulsion integrals are appreciably larger[20] in DSK than in MN and the same applies to the core- electron attractions and the core-core repulsions. On the other hand, for optimized parameters, the resonance integrals $\beta_{\mu\lambda}$ turn out to be smaller when using DSK rather than MN for the repulsion integrals. The relative magnitudes of the diagonal and nondiagonal elements of the core Hamiltonian matrix are consequently different in the two cases, the nondiagonal elements being more important in the Mataga-Nishimoto approximation.

Comparing the results for optimized parameters, we find similarly good predictions for most properties. Dipole moments of hydrocarbons are better reproduced by MN, but DSK is better for ionization potentials and MO orderings. Heats of formation are usually predicted somewhat better by DSK, particularly in the case of three-membered rings where the MN values are too negative. On balance, the DSK results seemed superior so we adopted the DSK approximation for calculating the two-center repulsion integrals.[41]

As for the core-electron attractions, several expressions for the function $f_2(R_{AB})$ in (16) were found that could be parametrized to give reasonable results for hydrocarbons. For systems with heteroatoms, however, the use of these expressions led to unrealistic charge distributions with highly polar bonds. This is not surprising because the core-electron attractions $V_{\mu\mu,B}$ appear in the diagonal elements of the Fock matrix. The function $f_2(R_{AB})$ consequently leads to unrealistic changes in the electronegativity of atoms in a molecule. We therefore decided to set

$$f_2(R_{AB}) = 0 \tag{20}$$

and to include the net electrostatic repulsion between neutral atoms in the expression for the core-core repulsion.

The functions $f_3(R_{AB})$ and $f_4(R_{AB})$ in the formulas for the core-core repulsions and resonance integrals, respectively, each contain adjustable parameters that refer to the pair of atoms (A,B) in question. In MINDO,[14-16] pair parameters are used, i.e., parameters characteristic of the atom pair involved. An alternative procedure, used, e.g., in CNDO,[5] is to replace the pair terms in f_3 and f_4 by appropriate combinations of terms containing atomic parameters, i.e., parameters characteristic of individual atoms. This approach was tried in MINDO but abandoned because it seemed to lead to inferior results. In our work in NDDO, we tried a number of functions of both kinds, including those used in MINDO/3. To our surprise, the results using atomic parameters were generally comparable in quality with those using pair parameters. Only a few relatively trivial cases were found (e.g., bond lengths of OO bonds) where the use of pair parameters represented a notable improvement.

Other things being equal, the use of atomic parameters is clearly preferable. In the first place the total number of parameters is less for sets of three or more atoms and the difference increases with the size of the set. Second, in the case of atomic parameters, only five additional parameters are needed to include an extra atom and these can be determined from data for molecules containing it in combination with any of the atoms already parametrized. In the case of pair parameters, the number of parameters needed to include an extra atom is much greater and they can be determined only if data are available for molecules containing the new atom in combination with all the atoms already parametrized. Third, one may reasonably expect atomic parameters to vary uniformly with the position of atoms in the periodic table. Good approximations to the parameters for new atoms should then be obtainable by interpolation or extrapolation from values for atoms already parametrized. As indicated above, the parametrization procedure is greatly simplified if good initial guesses for the values of the parameters are available.

In view of these considerations and in view of the relatively small advantages that pair parameters seemed to offer, we

Table III. Optimized MNDO Parameters

Parameter	H	B	C	N	O	F
U_{ss}, eV	−11.906 276	−34.547 130	−52.279 745	−71.932 122	−99.643.09	−131.071 548
U_{pp}, eV		−23.121 690	−39.205 558	−57.172 319	−77.797 472	−105.782 137
ζ, au	1.331 967	1.506 801	1.787 537	2.255 614	2.699 905	2.848 487
β_s, eV	−6.989 064		−18.985 044			−48.290 460
		−8.252 054		−20.495 758	−32.688 082	
β_p, eV			−7.934 122			−36.508 540
α, Å^{-1}	2.544 134	2.134 993	2.546 380	2.861 342	3.160 604	3.419 661

Table IV. Derived MNDO Parameters

Parameter	H	B	C	N	O	F
$H_f{}^A$, kcal mol^{-1}	52.102	135.70	170.89	113.00	59.559	18.86
$E_{el}{}^A$, eV	−11.906 276	−64.315 950	−120.500 606	−202.581 201	−317.868 506	−476.683 781
D_1, Å		0.506 893	0.427 284	0.338 616	0.282 894	0.268 138
D_2, Å		0.430 113	0.362 563	0.287 325	0.240 043	0.227 522
ρ_0, Å	0.560 345	0.679 822	0.588 660	0.529 751	0.466 882	0.425 492
ρ_1, Å		0.539 446	0.430 254	0.337 322	0.275 822	0.243 849
ρ_2, Å		0.476 128	0.395 734	0.324 853	0.278 628	0.255 793

decided to use atomic parameters for $f_3(R_{AB})$ and $f_4(R_{AB})$ in MNDO.

For the net electrostatic repulsion between two neutral atoms, we chose:

$$f_3(R_{AB}) = Z_A Z_B(s^A s^A, s^B s^B)[e^{-\alpha_A R_{AB}} + e^{-\alpha_B R_{AB}}] \quad (21)$$

α being an adjustable atomic parameter. Equation 21 is purely empirical, but it shows the correct behavior in the limit $R_{AB} \rightarrow \infty$ where $f_3(R_{AB})$ vanishes. For the pairs N-H and O-H, it was found advantageous to use a slightly modified expression[42]

$$f_3(R_{XH}) = Z_X Z_H(s^X s^X, s^H s^H)[(R_{XH}/\text{Å})e^{-\alpha_X R_{XH}} + e^{-\alpha_H R_{XH}}] \quad (X = N, O) \quad (22)$$

the numerical values of the α parameters in eq 21 and 22 being the same for each element.

The function $f_4(R_{AB})$ in the expression for the resonance integral $\beta_{\mu\lambda}$ (see eq 18) was chosen to be:

$$f_4(R_{AB}) = (\beta_\mu{}^A + \beta_\lambda{}^B)/2 \quad (23)$$

where $\beta_\mu{}^A$ is an adjustable parameter characteristic of AO ϕ_μ at atom A. For a given first-row element, there are at most two different β parameters, i.e., $\beta_s{}^A$ for the s AO and $\beta_p{}^A$ for the p AO. For carbon, the results were improved significantly by optimizing $\beta_s{}^C$ and $\beta_p{}^C$ separately, whereas for nitrogen and oxygen the two parameters could be set equal without impairing the quality of the results:

$$\beta_s{}^X = \beta_p{}^X \quad (X = N, O) \quad (24)$$

A final problem was to decide whether to use the same or different orbital exponents ζ_s and ζ_p for the s and p AO's of a given element. In optimizations where both were treated as adjustable parameters they usually converged to similar values. We therefore decided to set them equal to one another for each element.

$$\zeta_s{}^X = \zeta_p{}^X = \zeta^X \quad (X = C, N, O) \quad (25)$$

This completes the description of the approximations and parametric functions used in the MNDO method, and we can now turn to the numerical values of the parameters.

(V) MNDO Parameters

Table III lists the optimized values of the MNDO parameters for the elements H, B, C, N, O, and F. For convenience, parameters for B and F are included from later papers[43,44] in this series. The number of adjustable parameters for these elements is reduced from 61 in MINDO/3 to 31 in MNDO, due to the use of atomic instead of bond parameters.

The optimized one-center energies U_{ss} are quite close to Oleari's[23] values, but our U_{pp} parameters are consistently smaller. The optimized Slater exponents ζ seem rather large, although they are not much greater than weighted averages of the s and p exponents in MINDO/3. In the parameterization, we usually used smaller exponents as our initial guess. However the optimization then led to the larger values reported here.

Comparing the optimized parameters for different elements, it seems remarkable that they change quite regularly in the series C, N, O (cf. the values for the Slater exponents and for the α parameters). Indeed, it was possible to guess reasonable parameters for boron,[43] fluorine,[44a] and beryllium[44b] by extrapolation.

Apart from the optimized parameters in Table III, the MNDO method makes use of some derived parameters which are either taken from experimental data or calculated from the optimized parameters. The values for the one-center repulsion integrals have been given previously[16,22] and those for the remaining derived parameters are listed in Table IV. The experimental heats of formation $\Delta H_f{}^A$ of the atoms are taken from the literature,[45] and the electronic energies $E_{el}{}^A$ of the atoms are calculated from single-determinantal wave functions in MNDO approximation. Both quantities are used in eq 8 to convert the total energy of a molecule into its heat of formation. Finally, the charge separations D_l and the additive terms ρ_l are evaluated as specified in our model for the two-center repulsion integrals.

(VI) Comparison of MNDO with MINDO/3

The main difference between the NDDO and INDO approximations lies in the treatment of the two-center repulsion integrals and the two-center core-electron attractions. NDDO provides a closer approximation to the full Fock matrix since it retains all two-center terms involving monoatomic differential overlap. It has been shown that the NDDO approximation is consistent with the neglect of the overlap integrals in the normalization of the eigenvectors.[7] It also leads to quite an accurate approximation for symmetrically orthogonalized basis orbitals,[46-48] which is not true for the INDO approximation. Clearly there is more theoretical justification for the use of NDDO than for INDO.

From a physical point of view, the INDO approximation takes into account only the monopole of a charge distribution, whereas the NDDO approximation includes the higher multipoles and their interactions in the treatment of the two-center terms. Thus the two-center electron–electron repulsions and core–electron attractions are spherically averaged in INDO, whereas in NDDO they show an angular dependence, due to the possible different orientations of the higher multipoles. In INDO, the directionality of chemical bonding is only represented in the resonance integrals $\beta_{\mu\lambda}$ while in NDDO it is also included in the two-center electron–electron repulsions and core–electron attractions. Therefore we would expect an NDDO-based method to be superior to an INDO-based method whenever directional effects play an important role in a molecule.

In the following paper,[49] detailed MNDO results will be given for a large number of molecules. These indicate that the average absolute error for most ground state properties is reduced by about one-half in passing from MINDO/3 to MNDO. Here we may note some particular areas where MNDO appeared consistently superior to MINDO/3 throughout our parametrization studies. Such improvements cannot be attributed to any special choice of parametric functions or to especially efficient parametrization. They must rather indicate areas where the superiority of MNDO is due to the superiority of the NDDO approximation.

The first area was concerned with heats of formation of unsaturated molecules. In MINDO/3, the calculated heats of formation of aromatic hydrocarbons were consistently too positive and those of compounds with triple bonds ($C\equiv C$, $C\equiv N$) too negative. Both these deficiencies are overcome in MNDO.

Second, the MINDO/3 heats of formation for molecules containing adjacent atoms with unshared pairs of electrons (e.g., $H_2\ddot{N}-\ddot{N}H_2$) were too negative and the corresponding bonds too short. These errors were attributed to the neglect of one-center overlap in the INDO approximation. As one would expect on this basis, the corresponding MNDO results are close to experiment.

Third, MINDO/3 bond angles were often subject to quite large errors. The MNDO values are very much better, particularly for angles at C or N. This difference can be attributed to the better treatment of directional effects in bonding in the NDDO approximation (see above).

Finally, the ordering of MO's in MNDO agrees much better with that deduced from photoelectron spectroscopy than that in MINDO/3. In particular, MNDO gives no spurious high-lying σ orbitals in the case of unsaturated compounds. This improvement is probably again due to the better description of directional effects in bonding, leading to a correspondingly better distinction between σ and π electrons, and to the better description of repulsions due to hybridization moments.

The theoretical advantages of NDDO over INDO therefore seem to be fully borne out by our studies. Since the time required for calculations by MNDO is only ca. 20% greater than for MINDO/3, it seems likely that MNDO will prove even more useful as an aid in interpreting chemical behavior.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 75-2749) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center. One of us (W.T.) thanks the Studienstiftung des deutschen Volkes for a postdoctoral fellowship.

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(39) Parametrizations with optimized geometries were terminated much earlier; this is feasible because the initial guess in these runs is obtained from a previous parametrization with fixed geometries, so that the parameters only need little adjustment.

(40) In tests, we treated the one-center repulsion integrals as adjustable parameters, but their values only changed very slightly during the optimization.

(41) It has been shown[20] that the trends in the semiempirical integrals in the DSK approximation are in better agreement with the analytical integrals than those in the MN approximation.

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Ground States of Molecules. 39. MNDO Results for Molecules Containing Hydrogen, Carbon, Nitrogen, and Oxygen

Michael J. S. Dewar* and Walter Thiel

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78741. *Received October 27, 1976*

Abstract: Heats of formation, molecular geometries, ionization potentials, and dipole moments are calculated by the MNDO method for a large number of molecules. The MNDO results are compared with the corresponding MINDO/3 results on a statistical basis. For the properties investigated, the mean absolute errors in MNDO are uniformly smaller than those in MINDO/3 by a factor of about 2. Major improvements of MNDO over MINDO/3 are found for heats of formation of unsaturated systems and molecules with NN bonds, for bond angles, for higher ionization potentials, and for dipole moments of compounds with heteroatoms.

(I) Introduction

In the preceding paper,[1] we have introduced the approximations and parameters of the MNDO method (modified neglect of diatomic overlap). Here we report MNDO results for heats of formation, molecular geometries, ionization potentials, and dipole moments of a large number of molecules and compare them with the corresponding MINDO/3 values.[2] All results in this paper were derived from single-determinantal MNDO calculations, without inclusion of configuration interaction (CI), and refer to molecular structures optimized by the Davidon-Fletcher-Powell method.[3]

(II) Heats of Formation

Tables I and II compare calculated and observed heats of formation for a set of 138 closed shell molecules, selected to represent as many bonding situations as possible and with emphasis on those which had presented problems in MINDO. The mean absolute error for these compounds is reduced from 11.0 kcal/mol in MINDO/3 to 6.3 kcal/mol in MNDO.

Here, and subsequently, we use average errors as a measure of accuracy, rather than standard deviations, because our compounds were not chosen at random. Indeed, in view of our deliberate inclusion of molecules that had proved especially "difficult" in previous studies, the errors reported here are certainly greater than they would have been for a randomly chosen set.

The main improvements of MNDO over MINDO/3, are found (Table I) in the case of aromatic systems, molecules with triple bonds (C≡C, C≡N), three-membered rings, globular polycylic compounds with five- or six-membered rings, and molecules with NN bonds. Some of these improvements (e.g., for unsaturated systems and NN bonds) are probably due to the inclusion of directional effects in the two-center MNDO electron-electron repulsions and core-electron attractions.[1]

Large errors in the MNDO heats of formation (10-20 kcal/mol) are encountered in three areas where MINDO/3 met with similar difficulties. Four-membered rings are consistently predicted too stable and sterically crowded molecules with adjacent methyl groups (e.g., *tert*-butyl compounds) too unstable, while molecules with NO bonds show errors in both directions. The first two shortcomings (four-membered rings, sterically crowded molecules) seem to be inherent in the basic

Table I. Mean Absolute Errors $\Delta(\Delta H_f)$ for Heats of Formation[a]

Class of compd	No.	$\Delta(\Delta H_f)$, kcal/mol MNDO	MINDO/3
All compounds	138	6.3	11.0
Hydrocarbons	58	6.0	9.7
With aromatic rings	5	1.7	12.1
With triple bonds	6	6.6	13.5
With three-membered rings[b]	8	5.2	11.7
With four-membered rings[b]	7	18.7[c]	8.6
Acyclic hydrocarbons	26	3.5	6.9
Cyclic hydrocarbons	32	8.0	11.9
Bicyclic hydrocarbons with 5- and 6-membered rings	5	2.9	22.3
Nitrogen compounds (CHN)	34	6.5	17.3
Amines	11	4.1	6.9
Cyanides	8	4.6	19.6
With NN bonds	11	8.1	29.5
Oxygen compounds (CHO)	39	5.2	6.8
Alcohols, ethers	12	4.3	5.7
Aldehydes, ketones	10	4.3	6.1
Acids, esters, anhydrides	9	3.2	6.8
With OO bonds	5	7.7	3.4
Nitrogen-oxygen compounds (CHNO)	7	14.8	15.4
All compounds excluding those with 4-membered rings, *tert*-butyl groups, or NO bonds	122	5.0	10.9

[a] Based on the results in Table II. [b] Including bicyclic compounds. Molecules containing three- and four-membered rings were counted in the class of four-membered rings only. [c] Excluding cubane, the mean absolute error reduces to 13.5 kcal/mol.