

the mechanisms were already known or limited to two alternatives, and calculations using the larger basis sets have been further limited to very small molecules. To be useful as a general chemical tool, it must be possible to study rather large systems in detail. This can require an enormous amount of computation.

A striking feature of the results in Table III is the relatively small difference between the errors given by the 3-21G and 6-31G* models and between the ones given by the three semiempirical procedures. The accuracies of all seem indeed to be limited by some common factor. Thermal energy seems the obvious candidate. As noted above, nearly all ab initio studies of reactions have been based on the assumption that the thermal energy of a molecule is an additive function of the atoms in it, so that a heat of reaction or activation can be equated to the corresponding difference in total energy between the reactants and the products or the transition state. The same assumption is made tacitly in our semiempirical methods, where allowance for thermal energy is included via the parametrization, so it applies generally to the results in Table III. Better results could undoubtedly be obtained by making specific allowance for the thermal energy, using

partition functions constructed from calculated vibration frequencies, etc..

One last point of interest should be noted. By using eq 5 in reverse, ab initio energies of molecules can be estimated from their experimental heats of formation, with an average error of only ± 0.01 au. This could be useful in the case of larger molecules where calculations by the better ab initio methods would be prohibitively expensive. Since these are believed to give energies reasonably close to the HF limit, an indication of the latter could be obtained simply, and at no cost, in this way. Such information would provide a useful indication of the level of accuracy of ab initio procedures relative to Hartree-Fock.

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AM1: A New General Purpose Quantum Mechanical Molecular Model¹

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Abstract: A new parametric quantum mechanical molecular model, AM1 (Austin Model 1), based on the NDDO approximation, is described. In it the major weaknesses of MNDO, in particular failure to reproduce hydrogen bonds, have been overcome without any increase in computing time. Results for 167 molecules are reported. Parameters are currently available for C, H, O, and N.

Introduction

The purpose of the work reported in this series of papers¹ has been the development of a quantitative quantum mechanical molecular model for chemists to use as an aid to experiment in their own research, in particular in studies of chemical reactions and reaction mechanisms. To be useful in this connection, such a procedure must be not only sufficiently accurate but also applicable to the molecules in which chemists are directly interested rather than confined to simple models. These requirements eliminated, and still eliminate, ab initio procedures because such procedures are too inaccurate and/or require far too much computing time.¹ Our approach has accordingly been to use an approximation simple enough for the desired calculations to be feasible, using currently available computers, and to upgrade the accuracy of the results by introducing parameters that can be adjusted to fit the results to experiment. In this way we have been able to develop² two effective models, MINDO/3³ and MNDO,⁴ which are being widely used.⁵ As the preceding paper¹ shows, the results from MINDO/3 and MNDO are generally comparable with those from ab initio methods that require at least 1000 times more computing time.

It should be emphasized that even MINDO/3 and MNDO are *too slow* for general use in chemistry, using currently available computers. Calculations of reaction mechanisms, using standard computers such as the DEC VAX 11-780, require excessive amounts of computer time for systems containing more than a dozen "heavy" atoms (i.e., other than hydrogen). While much larger systems can be treated using "state-of-the-art" computers, such as the CDC 205 or CRAY, this does not reduce the cost of the calculations, because while these are several hundred times faster than a VAX, the cost of computing time is also greater by an almost equally large factor. A 100-fold increase in the speed of computers, with no increase in the cost of computing time, will be needed to enable our procedures to achieve their full potential, particularly in projected applications to biochemistry and organometallic chemistry.

A major problem in studying reactions by *any* current theoretical model is the lack of experimental data for the intermediate sections of potential surfaces and for the geometries of transition states. Calculations for these consequently involve the extrapolation of an empirical⁶ procedure into areas where it has not been, and indeed cannot be, tested. Such an extrapolation is safer, the better the performance of the method in question in all areas where it can be tested. Confidence in a semiempirical procedure is moreover strengthened by demonstrations of its ability to reproduce experimental results unrelated to those used in determining the parameters in it. One of the major assets of MINDO/3 and

(1) Part 76 of a series of papers reporting the development and use of quantum mechanical molecular models. For part 75, see: Dewar, M. J. S.; Storch, D. M. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) Dewar, M. J. S. *J. Mol. Struct.* **1983**, 100, 41.

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

(4) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, 99, 4899, 4907.

(5) A total of 623 papers reporting MNDO calculations have been listed in *Chemical Abstracts* since 1980.

(6) The errors in energies calculated even by "state-of-the-art" ab initio methods are enormous by chemical standards, far too large for any conclusions to be drawn a priori from the results; see ref 1.

MNDO was their demonstrated ability to reproduce *all* ground-state properties⁷ of molecules of *all* kinds,¹⁵ including properties and types of molecules not used in parametrizing them.

MINDO/3 has proved very effective in studies of a wide variety of hydrocarbons.¹⁸ Problems arise, however, in the case of molecules containing heteroatoms because of the neglect of one-center overlap in the INDO approximation on which MINDO/3 is based. These problems are avoided in MNDO but at the expense of other weaknesses,⁴ in particular failure to reproduce hydrogen bonds, energies that are too positive for crowded molecules (e.g., neopentane) and too negative for ones containing four-membered rings, and activation energies that tend to be too large.

After several years of effort we have finally been able to develop a "third generation" treatment in which these errors have been largely corrected. In view of the terminological confusion that has arisen between our procedures and conventional semiempirical ones which, while using the same basic approximations (CNDO, INDO, etc.), are grossly inaccurate, we decided to adopt an entirely different name for the new procedure, i.e., Austin Model 1 (AM1). While AM1 has as yet been parametrized only for the "organic" elements (CHON), no problems should arise in extending it to other "MNDO" elements. Parameters for these will be reported in due course.

Development of AM1

Extensive earlier attempts to correct the errors in MNDO, indicated above, convinced us that they mostly had a common cause, i.e., a tendency to overestimate repulsions between atoms when at ca. their van der Waals distance apart. The obvious way to deal with this was to modify the core repulsion function⁴ (CRF) in MNDO. Since extensive attempts to find a suitable function of some other type failed, we decided to use a brute force approach, modifying the existing function by additional Gaussian terms. Now that we know the optimum form of the function, we hope in later versions to approximate it by one with fewer parameters. We believe that AM1, in its present form, probably represents about the best that can be achieved using the NDDO approximation as a basis, without specific allowance for the contributions of thermal energy. The CRF in it is as follows:

$$\text{CRF}(AB) = z_A z_B \gamma_{ss} [1 + F(A) + F(B)] \quad (1)$$

where

$$F(A) = \exp(-\alpha_A R_{AB}) + \sum_i K_{A_i} \exp[L_{A_i}(R_{AB} - M_{A_i})^2]$$

$$F(B) = \exp(-\alpha_B R_{AB}) + \sum_j K_{B_j} \exp[L_{B_j}(R_{AB} - M_{B_j})^2]$$

(7) Properties reproduced by MNDO include heats of formation,⁴ molecular geometries,⁴ dipole moments,⁴ ionization energies,⁴ electron affinities,⁸ polarizabilities,⁹ molecular vibration frequencies,¹⁰ thermodynamic properties,¹¹ kinetic isotope effects,¹² properties of polymers,¹³ and ESCA chemical shifts.¹⁴

(8) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 784.

(9) Dewar, M. J. S.; Yamaguchi, Y.; Suck, S. H. *Chem. Phys. Lett.* **1978**, *59*, 541.

(10) Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Thiel, W.; Yamaguchi, Y. *J. Mol. Struct.* **1978**, *43*, 135.

(11) Numerous calculations have shown that the results from MNDO are at least as good as those from MINDO/3. For the latter, see: Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 7822.

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

(13) (a) Dewar, M. J. S.; Yamaguchi, Y.; Suck, S. H. *Chem. Phys.* **1979**, *43*, 145. (b) Dewar, M. J. S.; Stewart, J. J. P., work in course of publication.

(14) Rzepa, H. S., unpublished work.

(15) While both MINDO/3 and MNDO were parametrized using data exclusively derived from normal closed-shell neutral molecules, they reproduce the properties of radicals,^{3,4} ions,^{3,4,9} carbenes,^{3,4} and "nonclassical" species (boron hydrides¹⁶ and carboranes¹⁷).

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

(17) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1980**, *19*, 2662.

(18) MINDO/3 also reproduces the energies of "nonclassical" carbocations surprisingly effectively. See: Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1977**, *99*, 7432.

Table I. AM1 Parameters

parameter	element			
	H	C	N	O
U_{ss}	-11.396 427	-52.028 658	-71.860 000	-97.830 000
U_{pp}		-39.614 239	-57.167 581	-78.262 380
ζ_s	1.188 078	1.808 665	2.315 410	3.108 032
ζ_p		1.685 116	2.157 940	2.524 039
β_s	-6.173 787	-15.715 783	-20.299 110	-29.272 773
β_p		-7.719 283	-18.238 666	-29.272 773
α	2.882 324	2.648 274	2.947 286	4.455 371
K_1	0.122 796	0.011 355	0.025 251	0.280 962
K_2	0.005 090	0.045 924	0.028 953	0.081 430
K_3	-0.018 336	-0.020 061	-0.005 806	
K_4		-0.001 260		
L_1	5.000 000	5.000 000	5.000 000	5.000 000
L_2	5.000 000	5.000 000	5.000 000	7.000 000
L_3	2.000 000	5.000 000	2.000 000	
L_4		5.000 000		
M_1	1.200 000	1.600 000	1.500 000	0.847 918
M_2	1.800 000	1.850 000	2.100 000	1.445 071
M_3	2.100 000	2.050 000	2.400 000	
M_4		2.650 000		

The symbolism is the same as that in MNDO.⁴ The values of the L parameters (which determine the widths of the Gaussians) were not critical so a common value was used for most of them. They were not included in the overall optimization. The M and K parameters were all optimized. Note that the Gaussian terms, like the others in the CRF, refer to individual atoms, not pairs of atoms.

In MNDO, parameters were determined first for hydrocarbons (C, H), and other elements were then added one at a time. We had to do this because the number of molecules that could be included in the basis set for parametrization was limited by the computing time required. Development¹⁹ of a greatly improved optimization procedure has made possible the use of a much larger basis set, allowing parameters for C, H, O, and N to be optimized in a single operation with a basis set which included some CHON species.

Two strategies were used to modify the CRF and reduce excessive interatomic repulsions at large separations. In the first, one or more attractive Gaussians were added to compensate the excessive repulsions directly, centered in the region where the repulsions were excessive. In the second, repulsive Gaussians were centered at smaller internuclear separations, leading to an overall reduction of the main term in the expression for the core repulsion and hence reducing the repulsion at larger internuclear distances. In the case of carbon, hydrogen, and nitrogen, both types of Gaussian were included, while only repulsive Gaussians were needed for oxygen. Attempts to use only repulsive Gaussians for the other elements led to poorer results while use of attractive Gaussians alone led to no improvement over MNDO.

This kind of modification is by no means subtle, and indeed Burstein and Isaev²⁰ have recently described a similar modification of MNDO which accommodates hydrogen bonds, specific extra Gaussian terms being added for the pairs of atoms forming such bonds. Such ad hoc additions of terms could of course be made to correct errors in MNDO for *any* specific interactions in *any* molecule or molecules but only at the expense of undermining its validity as a general molecular model. For reasons indicated above, a procedure of this kind can be useful in chemistry only if the same parameters are used throughout, without reference to the structures of the individual molecules to which it is being applied.

It should perhaps be emphasized that the development of an effective treatment of this kind is *not* a trivial matter. Parametrization is still a purely empirical affair. All our attempts to develop theories that might help in the choice of parametric functions and parameters have failed. In the present study, each choice of Gaussians had to be tested by a complete reparam-

(19) Stewart, J. J. P., unpublished work.

(20) Burstein, K. Ya.; Isaev, A. N., *Theor. Chim. Acta* **1984**, *64*, 397.

Table II. Comparison with Experiment of Heats of Formation (ΔH_f ; kcal/mol) Calculated for Closed-Shell Molecules by Various Procedures

molecule	ΔH_f		error in ΔH_f				molecule	ΔH_f		error in ΔH_f			
	expt ^a	AM1	AM1	MNDO	3-21G	6-31G		expt ^a	AM1	AM1	MNDO	3-21G	6-31G
hydrogen	0.0	-5.2	-5.2	0.7	-9.5	-7.2	pyridine	34.6	32.1	-2.6	-5.7		
methane	-17.8	-8.8	9.0	5.9	-0.9	0.5	pyridazine	66.5	55.3	-11.2	-22.9		
ethane	-20.04	-17.4	2.6	0.3	0.2	1.9	pyrimidine	46.8	43.9	-2.9	-11.8		
ethylene	12.54	16.5	4.0	3.1	-1.6	-2.4	pyrazine	46.9	44.5	-2.4	-9.1		
acetylene	54.5	54.8	0.3	3.4	-1.7	-8.0	aniline	20.8	20.7	-0.1	1.2		
propane	-25.0	-24.3	0.7	0.1	0.4	1.9	hydrogen cyanide	32.3 ^b	31.0	-1.3	3.0	8.8	1.2
propene	4.8	6.6	1.8	0.2	1.9	-2.3	acetonitrile	15	19.3	4	4	13.8	5.3
propyne	44.2	43.4	-0.8	-2.8	0.4	-6.0	propionitrile	12.3	13.0	0.7	1.5		
allene	45.5	46.1	0.6	-1.6	-2.6	-6.8	acrylonitrile	43.2	45.0	1.8	0.7		
<i>n</i> -butane	-30.0	-31.1	-1.1	0.3			maleonitrile	81.3	76.0	-5.3	-6.6		
isobutane	-32.0	-29.4	2.6	5.2			cyanogen	73.3	67.9	-5.4	-6.7	22.4	
but-1-ene	-0.1	0.4	0.5	0.5			dicyanoacetylene	126.5	119.8	-6.7	-15.1		
<i>trans</i> -2-butene	-2.75	-3.3	-0.6	-2.4	-3.1		benzotrile	51.6	53.4	1.8	0.4		
<i>cis</i> -2-butene	-1.69	-2.2	-0.5	-2.7			methyl isocyanide	39	50.4	11	21	8.0	
isobutene	-4.0	-1.2	2.8	2.0	-3.9		hydrazine	22.8 ^b	13.7	-9.1	-8.6	7.6	-1.9
1,2-butadiene	38.8	37.1	-1.7	-5.2			methylhydrazine	22.6 ^b	17.0	-5.6	-6.5		
<i>trans</i> -1,3-butadiene	26.3	29.9	3.6	2.7	-4.7		1,1-dimethylhydrazine	20.1	23.8	3.7	-1.7		
1-butyne	39.5	37.5	-2.0	-3.3			1,2-dimethylhydrazine	22	21.6	0	-7		
2-butyne	34.8	32.0	-2.8	-9.9	0.4		<i>cis</i> -diimine	50.9 ^b	32.4	-18.5	-17.2	-7.9	-3.7
vinylacetylene	72.8 ^b	67.9	-4.9	-7.2			azo- <i>n</i> -propane	12.3	13.7	1.4	-8.2		
diacetylene	113.0 ^b	106.1	-6.9	-9.8	1.4		diazomethane	71.0 ^b	62.7	-8.4	-3.7		
<i>n</i> -pentane	-35.09	-37.9	-2.9	0.7			diazirene	79.0 ^b	86.8	7.8	-6.6		
neopentane	-40.15	-32.8	7.4	15.6			hydrogen azide	70.3 ^b	75.9	5.6	2.8	-17.3	
<i>trans</i> -1,3-pentadiene	18.2	19.9	1.6	0.6			oxygen	22.0 ^b	0.7	-21.3	-9.9	-2.4	-1.1
<i>cis</i> -1,3-pentadiene	19.4	21.0	1.5	0.7			ozone	34.2 ^b	37.8	3.6	14.3	-28.6	-24.4
1,4-pentadiene	25.2	25.0	-0.2	0.0			water	-57.8 ^b	-59.2	-1.4	-3.1	-4.6	-2.8
cyclopropane	12.7	17.8	5.1	-1.5	-8.4	-2.4	methanol	-48.16	-57.0	-8.8	-9.2	5.3	5.0
<i>cis</i> -dimethylcyclopropane	1.3 ^b	4.9	3.6	-3.1			ethanol	-56.21	-62.7	-6.5	-6.8	5.4	
cyclopropene	66.2	74.8	8.6	2.1	-18.4	-10.1	1-propanol	-60.98	-70.6	-9.6	-6.5		
1-methylcyclopropene	58.2	64.7	6.5	-4.5			2-propanol	-65.19	-67.7	-2.5	0.0		
1,2-dimethylcyclopropene	46.4 ^b	54.6	8.2	-7.2			<i>t</i> -butyl alcohol	-74.7	-71.6	3.1	10.4		
methylenecyclopropane	47.9	47.7	-0.2	-10.0			dimethyl ether	-44.0	-53.2	-9.2	-7.2	11.6	10.2
cyclobutane	6.8	0.2	-7.8	-18.7			diethyl ether	-60.3	-64.4	-4.1	-1.7		
cyclobutene, C _{2v}	37.5	45.8	8.3	-6.5	-11.2		oxirane	-12.6	-8.9	3.6	-2.9		
1,2-dimethylcyclobutene	19.8 ^b	27.0	7.2	-13.3			furan	-8.31	3.0	11.3	-0.3		
methylenecyclobutane	29.1	25.1	-4.0	-18.2			phenol	-23.0	-22.2	0.8	-3.7		
cyclopentane	-18.3	-28.8	-10.5	-12.0			anisole	-16.2	-15.8	0.4	-1.5		
cyclopentene	8.3	3.0	-5.3	-8.6			hydrogen peroxide	-32.5 ^b	-35.3	-2.8	-5.7	18.6	3.1
cyclopentadiene	32.1	37.1	5.0	0.0			dimethyl peroxide	-30.0	-27.0	3.0	1.9		
fulvene	47.5 ^b	62.7	15.2	6.2			diethyl peroxide	-46.1	-38.4	7.7	7.2		
cyclohexane	-29.49	-38.5	-9.0	-5.3			carbon monoxide	-26.4 ^b	-5.7	20.7	20.5	9.2	13.5
cyclohexene	-1.2	-10.0	-8.8	-8.7			carbon dioxide	-94.1 ^b	-79.8	14.3	19.0	7.4	15.7
1,3-cyclohexadiene	25.4	17.6	-7.8	-10.8			carbon suboxide	-22.4 ^b	-14.6	7.8	-1.1		
benzene	19.8	22.0	2.2	1.5	-2.7		formaldehyde	-25.9	-31.5	-5.6	-7.0	3.6	7.8
toluene	12.04	14.5	2.4	1.6			acetaldehyde	-39.7	-41.6	-1.9	-2.6	3.5	7.8
ethylbenzene	7.15	8.8	1.5	1.6			propionaldehyde	-44.4	-48.0	-3.7	-2.5		
styrene	35.4	38.8	3.3	2.6			acetone	-51.94	-49.2	2.7	2.5	4.1	
cycloheptatriene	43.2	38.3	-4.9	-9.4			ketene	-11.4	-5.7	5.7	4.6		
bicyclobutane	51.9	78.1	26.2	12.2			glyoxal	-50.7	-58.7	-8.0	-10.7		
spiropentane	44.3	50.5	6.2	-10.6			biacetyl	-78.2	-74.0	4.1	-0.1		
bicyclopropyl	30.9	39.6	8.7	-2.2			acetylacetone	-91.0	-85.5	5.5	7.7		
bicyclo[2.1.0]pentane	37.3 ^b	46.1	8.8	-7.1			<i>p</i> -quinone	-29.4	-25.0	4.3	-3.5		
norborane	-13.1	-14.4	-1.3	2.8			benzaldehyde	-8.8	-8.9	-0.1	-0.8		
norbornadiene	58.8	67.8	9.0	4.4			formic acid	-90.5	-97.4	-6.9	-2.1	11.3	
bicyclo[2.2.2]octane	-23.7	-36.0	-12.3	-2.6			acetic acid	-103.4	-103.0	0.4	2.3		
naphthalene	35.9	40.6	4.7	2.5			propionic acid	-108.4	-108.0	-0.4	2.2		
adamantane	-32.2	-42.7	-10.5	5.9			oxalic acid	-173	-172.4	1	-2		
cubane	148.7	151.2	2.5	-49.6			benzoic acid	-70.3	-68.0	2.3	4.6		
nitrogen	0.0	11.2	11.2	8.3	1.9	7.3	methyl formate	-85.0	-91.0	-6.0	-0.5		
ammonia	-11.0 ^b	-7.3	3.7	4.6	-1.0	-4.2	methyl acetate	-98.4	-96.4	2.0	4.9		
methylamine	-5.5	-7.4	-1.9	-2.0	3.2	0.0	acetic anhydride	-136.1	-142.8	-6.7	3.7		
dimethylamine	-4.4	-5.6	-1.2	-1.2	5.2	1.9	maleic anhydride	-95	-76.3	19	6.7		
trimethylamine	-5.7	-1.7	4.0	2.9			formamide	-44.5 ^b	-44.7	-0.3	5.1		
ethylamine	-11.3	-15.1	-3.8	-1.9			dimethylformamide	-45.8	-36.9	8.9	8.8		
<i>n</i> -propylamine	-16.8	-22.1	-5.3	-1.4			nitrous oxide	19.6 ^b	28.5	8.9	11.4	-15.2	-3.7
isopropylamine	-20.0	-19.2	0.8	3.8			nitrous acid	-18.8 ^b	-39.4	-20.6	-21.9	-3.6	
<i>tert</i> -butylamine	-28.90	-21.2	7.7	13.5			nitric acid	-32.1 ^b	-37.3	-5.2	14.8		
acetaldehyde imine	30.2	33.1	2.9	-5.1			methyl nitrite	-15.9	-31.8	-15.9	-20.8		
pyrrole	25.9	39.9	14.0	6.6			nitromethane	-17.7	-9.9	7.8	21.0		

^aexcept where noted, standard heats of formation at 25 °C: Pedley, J. B.; Rylance, G. "Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds", Sussex University, 1977. ^bFor references, see: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977 99, 4907.

trization for the basis set, followed by tests of the results by calculations for a much larger selection of molecules, chosen to include bonding of all kinds, and molecular species of all kinds,

and also some basic reactions. This approach, for which we have found no effective substitute, needs infinite patience and enormous amounts of computer time.

Table III. Comparison of Mean Absolute Errors for AM1, MNDO, and MINDO/3

average error in:	no. of com- pounds	MINDO/ 3		
		AM1	MNDO	
heats of formation (kcal/mol)				
(a) hydrocarbons	58	5.07	5.87	9.7
(b) species containing N and/or O	80	5.88	6.64	11.69
dipole moments (D)				
(a) hydrocarbons	11	0.17	0.25	0.26
(b) species containing N and/or O	46	0.26	0.32	0.54
ionization energies (eV)				
(a) hydrocarbons	22	0.29	0.39	0.31
(b) species containing N and/or O	29	0.40	0.55	1.02

Parameters

As indicated above, the formalism used in AM1 is essentially the same as in MNDO, with the exception of the CRF. The one-center electron repulsion integrals (g_{ij} , h_{ij}) remain unchanged, having the values assigned by Oleari.²¹ The parameters optimized were U_{ss} , U_{pp} , ζ_s , ζ_p , B_s , and B_p , and the parameters (K_X , α , and M_X) involved in the CRF (see above).

The value of a model is not related to the number of parameters used nor to the results for molecules in the parameterization basis set. Instead we are interested in its ability to correctly handle new situations, chemical systems which are not in the data set used to develop and test the model. With this idea in mind we carried out a selective grid search²² of the parameter hypersurface to find what we now believe to be the global minimum. Part of the improvement in AM1 over MNDO is due to the fact that a better minimum was found, corresponding in particular to different orbital exponents, which have a large effect on activation barriers, and to the ratios of the B parameters for s and p AOs, which appear to control the bond angles. Since the results for oxygen and nitrogen were little affected by changes in U_{ss} , we set them at the Oleari²¹ values. Likewise B_s and B_p for oxygen were set equal to ensure good bond angles for oxygen compounds.

Table I lists the final values of the parameters.

Results and Discussion

A. Heats of Formation of Neutral Closed-Shell Molecules.

Table II compares with experiment the heats of formation of the 138 molecules included in our standard tests. The third and fourth columns compare the errors in heats of formation from two ab initio models derived in the preceding paper.¹ The results from MNDO and AM1 are summarized in Table III which shows the average (unsigned) errors for the 58 hydrocarbons and 80 molecules containing nitrogen and/or oxygen.

Note that the AM1 errors for neopentane and *tert*-butylamine are all much less than those from MNDO. Clearly there has been a major improvement in the treatment of crowded molecules. Similar remarks apply to molecules containing four-membered rings, where the AM1 values are now reasonable. The improvement is dramatic in the case of cubane.

The only major AM1 errors for hydrocarbons are for fulvene and bicyclobutane, both of which resisted attempts to eliminate them. The results for *n*-paraffins indicate that the CH_2 increment is in error by ca. -1.9 kcal/mol. AM1 performs well for olefins and acetylenes, being much better than MNDO in the case of conjugated acetylenes. Cyclopentane and cyclohexane are both too stable, as would be expected in view of the too negative CH_2 increment.

The AM1 values for the nitrogen compounds are, overall, somewhat better than those from MNDO. The AM1 error for pyrrole is larger than in MNDO. However, the AM1 error for

Table IV. Comparison with Experiment of AM1 and MNDO Heats of Formation (ΔH_f° ; kcal/mol) for Cations

cation	ΔH_f°		error	
	obsd ^a	AM1	AM1	MNDO
methyl cation	260	252	-8	-16
ethyl cation (classical)	219	217	-2	1
2-propyl cation	192	192	0	9
<i>tert</i> -butyl cation	176	175	-1	11
ethylene radical cation	266	262	-4	0
allyl cation	226	226	0	-5
tropylium	209	210	1	-1
benzyl cation	216	222	6	2
NH_4^+	155	151	-4	10
CH_2NH_2^+	178	176	-2	9
OH_3^+	139	144	5	-5
HCO^+	199	188	-11	-14
$\text{CH}_2=\text{OH}^+$	167	161	-6	-11
NO_2^+	233	221	-12	8
NO^+	237	228	-9	-6

^aFor references, see: Dewar, M. J. S.; Thiel, W. J. *Am. Chem. Soc.* 1977 99, 4907.

Table V. Heats of Formation (ΔH_f° ; kcal/mol) for Neutral Radicals

radical	ΔH_f°		error	
	expt ^a	AM1	AM1	MNDO
$\text{CH}_3\cdot$	34.8	31.25	-3.6	-9.0
$\text{C}_2\text{H}_5\cdot$	25	15.48	-10	-12
$\text{C}_3\text{H}_7\cdot$	16.8	10.07	-6.7	-15.3
$\text{C}_4\text{H}_9\cdot$	4.5	-2.66	-7.2	-11.7
$\text{C}_2\text{H}_3\cdot$	59.6	64.78	5.2	4.1
$\text{C}_3\text{H}_5\cdot$	40	38.58	-1	-5
$\text{NH}_2\cdot$	40.1	38.41	-1.7	-3.0
$\text{CH}_3\text{NH}\cdot$	37	34.12	-3	-4
$\text{OH}\cdot$	9.5	1.07	-8.4	-9.0
$\text{CH}_3\text{O}\cdot$	-0.5	-3.54	-3.0	0.6
$\text{HCO}\cdot$	10.4	-0.72	-11.1	-10.9
$\text{NO}\cdot$	21.6	1.38	-20.2	-21.8
$\text{NO}_2\cdot$	7.9	-14.68	-22.6	-12.5
$\text{N}_3\cdot$	99	107.4	8.4	3

^aFor references, see: Dewar, M. J. S.; Thiel, W. J. *Am. Chem. Soc.* 1977 99, 4907.

pyridazine is less, and the errors for pyrimidine and pyrazine much less, than in MNDO. Simple nitrates are also reproduced better by AM1 while the error for methyl isocyanide, although large, is also much less than in MNDO.

The AM1 errors for oxygen-containing compounds are somewhat larger than those for nitrogen-containing ones or hydrocarbons, as was also the case in MNDO. Singlet oxygen ($^1\Delta_g \text{O}_2$) is much too stable and carbon monoxide much too unstable. Clearly AM1, like MNDO, has problems with diatomic molecules (see also N_2). The error in ozone is, however, much less, suggesting that AM1, unlike MINDO/3 or MNDO, may be useful in studies of the mechanism of ozonization. Note in this connection the excellent results for peroxides. The error for carbon dioxide, while large, is much less than in MNDO although maleic anhydride is worse.

Turning now to molecules containing both nitrogen and oxygen, AM1 is seen to represent a very real improvement over MNDO, though the errors are still rather large. While MNDO gave a value for the heat of isomerization of methyl nitrite to nitromethane that was in error by 41.8 kcal/mol, this has been reduced in AM1 to 23.7 kcal/mol. The correction of nonbonded repulsions also shows itself in the geometries of nitrobenzene and benzaldehyde, both of which are (correctly) predicted to be planar by AM1. MNDO predicted the substituents to be orthogonal to the ring, presumably through overestimation of the repulsions between oxygen and the ortho hydrogen atoms.

B. Cations. Table IV shows similar comparisons with experiment of heats of formation calculated for a number of cations, using AM1 and MNDO. The AM1 values are clearly better. AM1 does, like MNDO, fail to make the π complex form of the ethyl cation more stable than the classical one. However, the error

(21) Oleari, L.; DiSipio, L.; DeMichelis, G. *Mol. Phys.* 1966, 10, 97.

(22) Zebisch, E. G. Ph.D. Dissertation, The University of Texas at Austin (in preparation).

Table VI. Heats of Formation (ΔH_f ; kcal/mol) for Anions

anion	ΔH_f		
	expt ^a	AM1	error
CH ₃ O ⁻	-36.0	-38.8	-2.8
C ₂ H ₅ O ⁻	-47.5	-45.8	-1.7
C ₆ H ₅ O ⁻	-40.5	-41.0	-0.5
HCOO ⁻	-106.6	-110.0	3.4
CH ₃ COO ⁻	-122.5	-116.0	6.5
CH ₃ NH ⁻	30.5	33.1	2.6
(CH ₃) ₂ N ⁻	24.7	22.4	-2.3
(1-pyrrolyl) ⁻	19.5	28.1	8.6
NCCH ₂ ⁻	24.1	30.8	6.7
O ₂ NCH ₂ ⁻	-26.4	-29.2	-2.8
C ₅ H ₅ ⁻	21.3	25.2	3.9
HO ⁻	-33.2	-14.1	19.1

^aBartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Academic Press: New York, 1979; Vol. II.

Table VII. Calculated Heats of Reaction for Formation of Hydrogen-Bonded and van der Waals Adducts

donor/acceptor	ΔH	donor/acceptor	ΔH
CH ₃ OH/H ₂ O	-2.7	C ₅ H ₅ N/H ₂ O	-2.9
H ₂ O/CH ₃ OH	-5.0	HCOOH/NH ₃	-2.0
H ₂ O/CO ₂	-2.5	HCOOH/HCOOH	-6.4
H ₂ O/CH ₂ O	-3.4	NH ₂ CHO/NH ₂ CHO	-7.8
NH ₃ /H ₂ O	-2.7	CO ₂ /CO ₂	0.0
H ₂ O/H ₂ O	-3.3	CH ₄ /CH ₄	-0.1

Table VIII. Rotational and Inversion Barriers (kcal/mol)

molecule	barrier		error	
	obsd ^a	AM1	AM1	MNDO
ethylene	65.0	65.93	0.9	-2.5
ethane	2.9	1.25	-1.7	-1.9
methylamine	2.0	1.29	-0.7	-0.9
methanol	1.1	1.04	-0.1	-0.4
HO-OH (cis)	7.0	6.90	0.0	-0.1
HO-OH (trans)	1.1	0.09	-1.0	-1.1
formamide	~20	10.11		
<i>n</i> -butane (gauche)	0.8	0.73	-0.1	
<i>n</i> -butane (eclipsed)	4-6	3.28		
nitrobenzene		6.50		
NH ₃ (inversion)	6	4.24	2	

^aFor references, see: Dewar, M.J.S.; Thiel, W. *J. Am. Chem. Soc.* **1977** *99*, 4907.

is less than that in MNDO and indeed is similar to that given by the 4-31G ab initio model (7.3 kcal/mol²³).

C. Radicals. Table V shows similar comparisons with experiment of heats of formation for radicals. Here AM1 is clearly much superior to MNDO. While the errors for NO and NO₂, and for the corresponding cations, are still large, these were to be expected, given the poor results for other diatomic molecules and given that CO₂ is isoelectronic with NO₂⁺.

D. Anions. Table VI compares heats of formation calculated by AM1 for a variety of anions with experiment. The agreement is very good except for HO⁻, where the AM1 value is far too positive, and the 1-pyrrolyl anion, where the error reflects that (14 kcal/mol) for pyrrole.

MNDO likewise gave a heat of formation for HO⁻ that was much too positive.²⁴ The error was attributed, undoubtedly correctly, to the failure of our procedures to allow for orbital expansion in atoms carrying large negative charges. It has been found²⁵ that ab initio methods reproduce the energies of anions

Table IX. First Ionization Potentials (IP; eV)

molecule	IP		error	
	expt ₁	AM1	AM1	MNDO
hydrogen	15.98	14.92	-1.06	-0.24
methane	13.60	13.31	-0.29	0.27
ethane	12.10 ^b	11.77	-0.33	0.6
ethylene	10.51	10.55	0.04	-0.33
acetylene	11.40	11.50	0.10	-0.37
propane	11.50	11.32	-0.18	0.80
propene	10.01	9.99	-0.02	-0.02
propyne	10.37	10.74	0.37	0.36
allene	10.07 ^b	10.14	0.07	-0.05
isobutane	11.40	11.29	-0.11	0.70
<i>trans</i> -1,3-butadiene	9.08	9.33	0.25	0.06
diacetylene	10.17	10.37	0.20	-0.17
neopentane	11.30	11.53	0.23	0.8
cyclopropane	11.00 ^b	11.48	0.48	0.4
cyclopropene	9.86	9.82	-0.04	0.03
cyclobutane	11.00 ^b	11.04	0.04	0.8
cyclobutene	9.43	9.72	0.29	0.34
cyclopentene	9.18	9.44	0.26	0.54
cyclopentadiene	8.57	9.09	0.52	0.47
benzene	9.24	9.65	0.41	0.15
toluene	8.78	9.33	0.55	0.50
naphthalene	8.15	8.71	0.56	0.42
nitrogen	15.60	14.32	-1.28	-0.72
ammonia	10.85	10.42	-0.43	0.34
methylamine	9.45 ^b	9.76	0.31	1.10
dimethylamine	8.93 ^b	9.36	0.43	1.11
trimethylamine	8.50	9.15	0.65	1.09
ethylideneimine	9.80	10.32	0.52	0.9
pyrrole	8.22	8.66	0.43	0.34
pyridine	9.59	9.93	0.34	0.10
hydrogen cyanide	13.60	13.68	0.08	-0.18
acetonitrile	12.20	12.47	0.27	0.60
acrylonitrile	10.91	10.86	-0.05	-0.29
propenenitrile	11.60	11.65	0.05	-0.24
cyanogen	13.36	13.31	-0.05	-0.14
ozone	12.75 ^b	13.10	0.35	-0.04
water	12.61	12.46	-0.15	-0.42
methanol	10.96	11.13	0.17	0.45
dimethyl ether	10.04	10.61	0.57	1.00
oxirane	10.57	11.33	0.76	0.92
furan	8.88	9.32	0.44	0.26
carbon monoxide	14.01	13.31	-0.70	-0.58
carbon dioxide	13.78	13.21	-0.57	-0.99
formaldehyde	10.89	10.78	-0.11	0.15
acetaldehyde	10.21	10.72	0.51	0.67
acetone	9.72	10.67	0.95	1.03
ketene	9.64	9.60	-0.04	-0.35
propenoaldehyde	10.11	10.69	0.58	0.58
glyoxal (trans)	10.59	10.66	0.07	0.16
formic acid	11.51	11.82	0.31	0.23
methyl formate	11.02	11.57	0.55	0.59

^aExcept where noted: Siegbahn, K.; Allison, D. A.; Allison, J. H. In "Handbook of Spectroscopy", Robinson, J. W., Ed; CRC Press: Cleveland Ohio, 1974; Vol. I, Section B. ^bFor references, see: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977** *99*, 4907.

only if diffuse AOs are included in the basis set. Use of a split basis set is likewise essential in calculations for cations to allow for orbital shrinkage with positive charge. Indeed, it seems surprising at first sight that the results from MNDO and AM1 for ions of both signs are normally so good, given that the parameters in both treatment were determined solely from data for neutral molecules and given that no provision is made in either for changes in AOs with atomic charge. However, the charges on atoms in neutral organic molecules can be quite large, judging by results both from AM1 or MNDO and from ab initio methods. The scheme used in MNDO and AM1 can evidently accommodate itself to such situations. Problems arise only when the charge on an atom approaches unity. Note that even a methyl group is sufficient to relieve the situation, the AM1 heat of formation for CH₃O⁻ agreeing well with experiment. In it the calculated formal charge on oxygen is 0.76.

E. Hydrogen Bonds. Table VII shows calculated (AM1) heats

(23) (a) Pople, J. A. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *17*, 1. (b) Lathan, W. A.; Curtiss, L. A.; Hehre, W. J.; Lisle, J. B.; Pople, J. A. *Prog. Phys. Org. Chem.* **1974**, *11*, 1.

(24) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 784.

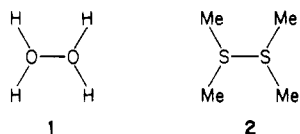
(25) (a) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609. (b) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363.

Table X. Higher Ionization Potentials (eV) from Koopmans' Theorem

	AM1	obsd ^a	orbital
COHH	10.56	10.51	1b _{1u}
	11.83	12.85	1b _{1g}
	14.30	14.66	2a _g
	15.80	15.87	1b _{2u}
C ₂ H ₂	11.50	11.40 ^b	1π _u
	15.45	16.36	2σ _g
	20.65	18.69	1σ _u
C ₆ H ₆	9.65	9.24 ^c	1e _{1g}
	11.89	11.49	2e _{2g}
	13.38	12.1	1a _{2u}
	14.16	13.8	2e _{1u}
	15.40	14.7	1b _{2u}
	16.12	15.4	1b _{1u}
	17.86	16.9	2a _{1g}
	18.83	11.81	2π _u
C ₄ H ₂	14.57	13.89	1π _u
	10.42	10.85	2a ₁
NH ₃	15.90	15.8	1e
	32.69	27.0	1a ₁
HCN	13.68	13.60 ^b	π
	13.99	14.0	3σ
	21.35	19.95	2σ
N ₂	14.32	15.60	X ² Σ _g
	16.19	16.98	A ² Π _u
	21.43	18.78	B ² Σ _u ⁺
NC ₄ N	10.37	10.17	1π _g
	13.31	12.62	π
H ₂ O	12.46	12.62	1b ₁
	14.96	14.74	2a ₁
	18.19	18.51	1b ₂
	36.42	32.2	1a ₁
CH ₂ O	10.78	10.88 ^b	2b ₂
	14.54	14.38	1b ₁
	16.26	16.00	2a ₁
	17.14	16.78	1b ₂

^aUnless otherwise noted, see Table IX, footnote a. ^bFor references, see: Dewar, M. J. S.; Thiel, W. J. *Am. Chem. Soc.* **1977** *99*, 4907. ^cAsbrink, L.; Edquist, O.; Linkholm, E.; Selin, L. E. *Chem. Phys. Lett.* **1970**, *5*, 192.

of formation from their components for some hydrogen-bonded species. While the AM1 values are too small, the errors are within the usual range for AM1 (see, e.g., Table II). Note in particular the small attractive interaction between two molecules of methane, which indeed is close to the heat of formation of the van der Waals dimer. Previous semiempirical treatments have reproduced hydrogen bonds, if at all, only spuriously, because of a prediction that molecules of all kinds attract one another. For example, CNDO/2 predicts⁵ water to form a dimer (1), with trivalent



oxygen, about equal in energy to the hydrogen-bonded dimer, while dimethyl sulfide is predicted to form a similar dimer (2) with a heat of reaction of -125 kcal/mol! AM1 predicts only a weak attraction between water molecules in the orientation indicated in 1. Thus the hydrogen bonds in AM1 are clearly genuine, even if they are weak. The weakness should not affect the calculation of geometries in reaction paths seriously, given that the errors are in the range expected in AM1.

F. Rotational Barriers. Table VIII shows analogous comparisons of AM1 and MNDO rotational barriers. The barriers to rotation about saturated single bonds, and the barrier to rotation in formamide, are underestimated in AM1, as they were in MNDO. Otherwise the AM1 values are very good.

G. Ionization Energies. Table IX compares with experiment the first ionization energies estimated from the HOMO energies given by AM1 and MNDO, using Koopmans' theorem. The agreement with experiment is visibly better for AM1, as is in-

Table XI. Dipole Moments (D)

molecule	dipole moment		error in	
	expt ^a	AM1	AM1	MNDO
propane	0.08	0.004	-0.08	-0.08
propene	0.37	0.23	-0.14	-0.33
propyne	0.78	0.40	-0.38	-0.66
cyclopropene	0.45	0.36	-0.09	0.03
cyclobutene	0.13	0.17	0.04	-0.05
cyclopentene	0.20	0.17	-0.03	-0.15
cyclopentadiene	0.42	0.53	0.11	-0.24
3,4-dimethylene-cyclobutene	0.62	0.21	-0.41	-0.40
fulvene	0.42	0.69	0.27	0.27
toluene	0.36	0.27	-0.09	-0.30
bicyclobutane	0.68	0.43	-0.25	-0.27
ammonia	1.47	1.85	0.38	0.29
methylamine	1.31	1.49	0.18	0.17
dimethylamine	1.03	1.23	0.20	0.14
trimethylamine	0.61	1.03	0.42	0.14
ethylamine	1.22	1.53	0.31	0.30
acetaldehyde imine	1.90	1.75	-0.15	-0.15
pyrrole	1.74	1.96	0.22	0.07
pyridine	2.22	1.98	-0.25	-0.25
aniline	1.53	1.54	0.01	-0.05
hydrogen cyanide	2.98	2.36	-0.62	-0.47
acetonitrile	3.92	2.89	-1.03	-1.29
acrylonitrile	3.87	3.00	-0.87	-0.90
propenenitrile	3.72	3.04	-0.68	-0.51
methyl isocyanide	3.85	2.82	-1.03	-0.51
methylhydrazine	1.66	2.17	0.51	-1.68
diazomethane	1.50	1.33	-0.18	-0.25
1,2-diazirene	1.59	1.63	0.04	-0.04
methyl azide	2.17	1.94	-0.23	-0.54
ozone	0.53	1.20	0.67	0.65
water	1.85	1.86	0.01	-0.07
methanol	1.70	1.62	-0.08	-0.22
ethanol	1.69	1.55	-0.14	-0.29
dimethyl ether	1.30	1.43	0.13	-0.04
diethyl ether	1.15	1.24	0.09	-0.06
oxirane	1.89	1.90	0.01	0.03
furan	0.66	0.50	-0.17	-0.24
phenol	1.45	1.24	-0.22	0.22
anisole	1.38	1.25	-0.13	0.06
carbon monoxide	0.11	0.06	-0.05	0.08
formaldehyde	2.33	2.32	-0.01	-0.17
acetaldehyde	2.69	2.69	0.00	-0.31
acetone	2.88	2.92	0.04	-0.37
ketene	1.42	1.34	-0.08	-0.38
propionaldehyde	3.12	3.06	-0.06	-0.19
propynoaldehyde	2.47	2.81	0.34	0.39
formic acid	1.41	1.48	0.07	0.08
acetic acid	1.74	1.89	0.15	-0.06
propionic acid	1.75	1.95	0.20	-0.11
methyl formate	1.77	1.51	-0.26	-0.14
methyl acetate	1.72	1.74	0.02	0.02
formamide	3.73	3.69	-0.04	-0.64
dimethylformamide	3.82	3.55	-0.27	-0.63
nitrous oxide	0.17	0.64	0.47	0.59
nitrous acid trans	1.86	2.31	0.45	0.41
nitrous acid cis	1.42	1.44	0.02	0.14
nitric acid	2.17	2.57	0.40	0.61

^aFor references, see: Dewar, M. J. S.; Thiel, W. J. *Am. Chem. Soc.* **1977** *99*, 4907.

dicated by the average errors (Table II).

AM1 shares with MNDO the ability to reproduce higher ionizations. Some examples are shown in Table X. While AM1 again tends to overestimate the energies of ionizations from orbitals with binding energies >18 eV, the errors are less than in the case of MNDO. As noted earlier, the errors occur in MOs derived largely from 2s AOs of C, N, or O. It was suggested previously that they are due to neglect of 1s-2s interactions in the core approximation used in MNDO and AM1. The results obtained here suggest, however, that the problem is due in part to the choice of the U_{ss} parameters.

H. Dipole Moments. Table XI compares with experiment dipole moments calculated by AM1 and MNDO. The AM1

Table XII. Bond Lengths (XY, Å), Bond Angles (XYZ, deg), and Dihedral Angles (WXYZ, deg)




molecule	geometrical parameters, calcd (obsd) ^a
H ₂	HH 0.667 (0.742)
CH ₄	CH 1.112 (1.094)
C ₂ H ₆	CC 1.501 (1.536), CH 1.117 (1.091), HCC 110.7 (110.9)
C ₂ H ₄	CC 1.325 (1.339), CH 1.098 (1.086), HCC 122.7 (121.2)
C ₂ H ₂	CC 1.195 (1.203), CH 1.061 (1.060)
C ₃ H ₈ (a)	CC 1.507 (1.526), C ¹ H ⁴ 1.117 (1.089), C ¹ H ⁵ 1.117 (1.094), C ² H ⁷ 1.123 (1.096), C ¹ C ² C ³ 111.8 (112.4), H ⁷ C ² H ⁸ 107.0 (106.1), H ⁴ C ¹ C ² 110.42 (111.8), H ⁵ C ¹ H ⁶ 108.2 (107.3), C ² C ¹ H ⁵ H ⁶ 121.4 (126.4)
H ₂ C=CHCH ₃ (a)	C ¹ C ² 1.331 (1.336), C ² C ³ 1.478 (1.496), C ¹ H ⁴ 1.097 (1.081), C ¹ H ⁵ 1.098 (1.091), C ² H ⁶ 1.103 (1.090), C ³ H ⁷ 1.117 (1.109), C ³ H ⁸ 1.119 (1.098), C ¹ C ² C ³ 123.9 (124.3), H ⁴ C ¹ C ² 122.5 (121.5), H ⁵ C ¹ C ² 122.8 (120.5), H ⁶ C ² C ¹ 121.3 (119.0), H ⁷ C ³ C ² 111.9 (111.2)
HC≡CCH ₃	H ⁸ C ³ H ⁹ 108.0 (106.2), C ² C ³ H ⁸ H ⁹ 120.0 (126.0)
CH ₃ C≡CH	C ¹ C ² 1.197 (1.206), C ² C ³ 1.427 (1.459), C ¹ H 1.060 (1.056), C ³ H 1.121 (1.105), C ² C ³ H 110.5 (110.2)
H ₂ C=C=CH ₂	CC 1.298 (1.308), CH 1.100 (1.087), HCH 115.4 (118.2)
n-C ₄ H ₁₀	C ¹ C ² 1.510 (1.533), C ² C ³ 1.514 (1.539), C ¹ C ² C ³ 111.6 (112.8)
i-C ₄ H ₁₀	CC 1.514 (1.525), CCC 110.7 (111.2)
CH ₃ CH=CHCH ₃	C ¹ C ² 1.475 (1.508), C ² C ³ 1.336 (1.347), C ¹ C ² C ³ 123.96 (123.8)
H ₂ C=C(CH ₃) ₂	C ¹ C ² 1.336 (1.330), C ² C ³ 1.483 (1.508), C ¹ C ² C ³ 122.4 (122.4)
H ₂ C=CHCH=CH ₂	C ¹ C ² 1.334 (1.341), C ² C ³ 1.451 (1.463), C ¹ C ² C ³ 123.5 (123.3)
H ₃ CC≡CCH ₃	C ¹ C ² 1.425 (1.444), C ² C ³ 1.198 (1.213), C ¹ H 1.121 (1.115), HC ¹ C ² 110.6 (110.7)
HC≡CCH=CH ₂	C ¹ C ² 1.198 (1.208), C ² C ³ 1.409 (1.431), C ³ C ⁴ 1.336 (1.341), C ² C ³ C ⁴ 124.3 (123.1)
HC≡CC=CH	C ¹ C ² 1.198 (1.205), C ² C ³ 1.357 (1.376), C ¹ H 1.060 (1.046)
C(CH ₃) ₄	CC 1.521 (1.539), CH 1.116 (1.120), HCC 110.3 (110.0)
cyclopropane	CC 1.501 (1.510), CH 1.104 (1.089), HCH 111.7 (115.1)
cyclopropene	C ¹ C ² 1.317 (1.296), C ² C ³ 1.490 (1.509), C ¹ H 1.069 (1.072), C ³ H 1.106 (1.088), HC ¹ C ² 151.9 (149.9), HC ³ H 111.5 (114.6)
cyclobutane	CC 1.545 (1.548), CH 1.109 (1.133), HCH 109.6 (108.1), CCCC 0.0 (153.0)
cyclobutadiene	C ¹ H 1.080 (1.083), C ³ H 1.109 (1.094), HC ¹ C ² 136.3 (133.5), HC ³ H 110.6 (109.2), C ¹ C ⁴ HH 131.7 (135.8)
cyclopentane	CC 1.521 (1.546), CH 1.116 (1.114), HCC 110.3 (111.7)
cyclopentadiene (a)	C ¹ C ² 1.359 (1.342), C ² C ³ 1.471 (1.469), C ¹ C ⁵ 1.509 (1.509)
fulvene	C ¹ C ² 1.483 (1.470), C ² C ³ 1.363 (1.355), C ³ C ⁴ 1.477 (1.476), C ¹ C ⁶ 1.332 (1.349)
cyclohexane	CC 1.515 (1.536), CH 1.121 (1.121), CCC 111.3 (111.4), HCH 107.4 (107.5), CCCC 55.1 (54.9)
cyclohexene	C ¹ C ² 1.334 (1.335), C ² C ³ 1.485 (1.504), C ³ C ⁴ 1.517 (1.515), C ⁴ C ⁵ 1.514 (1.550), C ¹ C ² C ⁴ C ⁵ 14.0 (28.3)
benzene	CC 1.395 (1.397), CH 1.100 (1.084)
bicyclobutane	C ¹ C ² 1.510 (1.498), C ¹ C ³ 1.494 (1.497), C ¹ H 1.080 (1.071), C ² H _{eq} 1.105 (1.093), C ² H _{ax} 1.104 (1.093), C ² C ³ C ¹ C ⁴ 122.0 (121.7)
spiropentane	C ¹ C ² 1.480 (1.469), C ² C ³ 1.507 (1.519), C ² 1.105 (1.091), HC ² H 112.5 (118.4), C ³ C ² H 145.7 (148.3)
housane (a)	C ¹ C ² 1.536 (1.528), C ² C ³ 1.557 (1.565), C ¹ C ⁴ 1.541 (1.536), C ¹ C ⁵ 1.505 (1.507), C ⁵ C ⁴ C ¹ C ² 114.6 (116.7)
norbornane	C ¹ C ² 1.542 (1.539), C ² C ³ 1.540 (1.557), C ¹ C ⁷ 1.550 (1.560), C ¹ C ⁷ C ⁴ 94.3 (93.1), C ⁶ C ¹ C ⁴ C ³ 112.0 (113.1)
norbornadiene	C ¹ C ² 1.531 (1.535), C ² C ³ 1.354 (1.343), C ¹ C ⁷ 1.576 (1.573), C ¹ C ² C ⁴ 92.7 (94.1), C ⁶ C ¹ C ⁴ C ³ 112.5 (115.6)
naphthalene	C ¹ C ² 1.373 (1.364), C ² C ³ 1.416 (1.415), C ¹ C ⁹ 1.422 (1.421), C ⁹ C ¹⁰ 1.421 (1.418)
N ₂	NN (1.094)
NH ₃	NH 0.998 (1.012), HNH 109.0 (106.7)
CH ₃ NH ₂	CN 1.432 (1.474), NH 1.004 (1.011), HNC 111.3 (112.0), HNH 109.0 (105.9)
HN(CH ₃) ₂	CN 1.437 (1.426), NH 1.003 (1.019), CNC 114.6 (112.2), HNC 109.0 (108.9), HNCC 126.3 (125.4)
N(CH ₃) ₃	CN 1.447 (1.451), CNC 112.8 (110.9)
azirane	CN 1.455 (1.475), CC 1.495 (1.481), NH 1.002 (1.016), HNCC 106.5 (112.5)
pyrrole	N ¹ C ² 1.391 (1.370), C ² C ³ 1.401 (1.382), C ³ C ⁴ 1.436 (1.417), N ¹ H 0.984 (0.996), C ² H 1.089 (1.076), C ³ H 1.085 (1.077), H ² CC ³ 130.0 (130.8), HC ³ C ² 126.8 (125.5)
pyridine	C ² N ¹ 1.347 (1.338), C ² C ³ 1.408 (1.394), C ³ C ⁴ 1.396 (1.392), C ² H 1.047 (1.086), C ³ H 1.096 (1.082), C ⁴ H 1.100 (1.081), C ⁶ N ¹ C ² 117.6 (116.9), N ¹ C ² C ³ 123.4 (123.8), C ² C ³ C ⁴ 118.3 (118.5), C ³ C ⁴ C ⁵ 118.9 (118.4), HC ² C ³ 120.8 (120.2), HC ³ C ² 120.5 (120.1)
HCN	CN 1.160 (1.154), CH 1.069 (1.063)
CH ₃ CN	CN 1.163 (1.157), CC 1.440 (1.458), CH 1.120 (1.104), HCC 110.1 (109.5)
CH ₂ =CHCN	C ¹ C ² 1.334 (1.339), C ² C ³ 1.420 (1.426), C ³ N 1.164 (1.164), C ¹ C ² C ³ 123.2 (122.6)
NCCN	CN 1.162 (1.154), CC 1.384 (1.389)
CH ₃ NC (a)	C ¹ N ² 1.395 (1.424), N ² C ³ 1.181 (1.166), C ¹ H 1.125 (1.101), HC ¹ N ² 110.1 (109.1)
H ₂ NNH ₂	NN 1.379 (1.449), NH 1.014 (1.022), HNN 107.2 (112.0), HNH 105.8 (106.0), HNNH 61.9 (90.0)
CH ₂ N ₂	CN 1.294 (1.32), NN 1.139 (1.12), CH 1.099 (1.08), HCH 121.2 (127)
O ₂	OO 1.087 (1.216)
O ₃	OO 1.160 (1.278), OOO 120.9 (116.8)
H ₂ O	OH 0.962 (0.957), HOH 103.4 (104.5)
H ₂ O ₂	OO 1.300 (1.475), OH 0.983 (0.950), HOO 105.9 (94.8), HOOH 128.3 (119.8)
CH ₃ OH (a)	C ¹ O ² 1.410 (1.425), O ² H ³ 0.964 (0.945), C ¹ H ⁴ 1.119 (1.094), C ¹ H ⁵ 1.119 (1.094), C ¹ O ² H ³ 107.2 (108.5), H ⁴ C ¹ O ² 105.1 (107.0), H ⁵ C ¹ H ⁶ 110.1 (108.6), O ² C ¹ H ⁵ H ⁶ 119.5 (129.8)
(CH ₃) ₂ O	CO 1.417 (1.410), COC 112.9 (111.7)
furan	O ¹ C ² 1.397 (1.362), C ² C ³ 1.397 (1.361), C ³ C ⁴ 1.447 (1.431), C ² H 1.085 (1.075), C ³ H 1.086 (1.077), HC ² O ¹ 114.3 (115.9), HC ³ C ⁴ 125.5 (128.0)
CO	CO 1.171 (1.128)
CO ₂	CO 1.189 (1.162)
CH ₃ O	CO 1.228 (1.208), CH 1.110 (1.116), HCH 115.6 (116.5)
CH ₃ CHO	C ¹ C ² 1.489 (1.501), C ² O 1.231 (1.216), C ² H 1.117 (1.114), C ¹ C ² O 123.5 (123.9), C ¹ C ² H 115.3 (117.5)
(CH ₃) ₂ CO	CC 1.495 (1.507), CO 1.236 (1.222), CCC 115.5 (117.2)
CH ₂ CO	C ¹ C ² 1.307 (1.314), C ² O 1.193 (1.161), C ¹ H 1.095 (1.085), HC ¹ H 117.2 (122.6)
(CHO) ₂	C 1.229 (1.207), CC 1.508 (1.525), CH 1.111 (1.116), OCC 121.0 (121.2), HCC 115.9 (112.2)
HCO ¹ O ² H	CO ¹ 1.230 (1.202), CO ² 1.356 (1.343), O ² H 0.972 (0.927), CH 1.103 (1.097), O ¹ CO ² 117.6 (124.9), CO ² H 110.6 (106.3), HCO ¹ 130.1 (124.1)
CH ₃ CO ¹ O ² H	CC 1.486 (1.520), CO 1.234 (1.214), CO 1.365 (1.364), OH 0.971 (0.97), CCO 129.4 (126.6), CCO 114.0 (110.6), COH 110.0 (107.0)
HCOOCH ₃	O ¹ C ² 1.230 (1.200), C ² O ³ 1.364 (1.334), O ³ C ⁴ 1.429 (1.437), O ¹ C ² O ³ 119.1 (125.9), C ² O ³ C ⁴ 117.3 (114.8)
N ₂ O	NN 1.128 (1.126), NO 1.175 (1.186)
HO ¹ NO ²	NO ² 1.157 (1.163), NO ¹ 1.319 (1.433), O ¹ H 0.974 (0.954), O ¹ NO ² 112.6 (110.7), NO ² H 107.0 (102.1)

Table XII (Continued)

molecule	geometrical parameters, calcd (obsd) ^a
HONO ₂ (a)	NO ¹ 1.186 (1.199), NO ² 1.195 (1.211), NO ³ 1.334 (1.406), O ³ H 0.983 (0.964), O ¹ NO ² 129.1 (113.9), O ¹ NO ³ 116.4 (115.9), NO ³ H 109.8 (102.2)
H ₂ NCHO (a)	CN 1.365 (1.376), CO 1.242 (1.193), CH ³ 1.117 (1.102), NH ¹ 0.990 (1.014), NH ² 0.986 (1.002), H ¹ NCO 0.1 (~7), H ² NCH ³ 0.4 (~-12)

^a For numbering of atoms and references, see: Dewar, M. J. S.; Thiel, W. J. *Am. Chem. Soc.* **1977** *99*, 4907.

Table XIII. Heats of Activation (kcal/mol)

reaction	heat of activation			
	obsd	AM1	MNDO	MINDO/3
CH ₃ · + HC=CH → CH ₃ CH=CH·	7.7 ^a	6.83	16.7	7.3
CH ₃ · + CH ₂ =CHCH ₃ → CH ₃ CH ₂ CHCH ₃ (CH ₃) ₂ CH·	7.4 ^b (c)	1.31 3.99	13.5 18.0	7.8 12.9
CH ₃ · + CH ₃ CH ₃ → CH ₄ + C ₂ H ₅ ·	11 ^a	11.96	27.2	6.1
:CHCH ₂ → CH ₂ =CH ₂	1-3	14.92	21.8	0.7
	4-5 ^d	22.17	39	28.2
	40 ± 6 ^e	61.57	90	63.2
	32.9 ^f	36.0		

^a Kerr, J. A.; Parsonage, M. J. "Evaluated Kinetic Data on Gas Phase Addition Reactions; Reactions of Atoms and Radicals with Alkenes, Alkynes, and Aromatic Compounds"; Butterworths: London, 1972. ^b Cvetzanovic, R. J.; Irwin, R. S. *J. Chem. Phys.* **1967**, *46*, 1694. ^c 10% of total product. ^d This value (Baughcum, S. L.; Smith, Z.; Wilson, E. B.; Duerst, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 2260) is probably low, due to neglect of tunneling. Ab initio estimates range from 6.6 to 11.5. ^e Kwart, H.; Latimare, M. C. *J. Am. Chem. Soc.* **1971**, *93*, 3770. ^f (a) Cooper, W.; Walters, W. D. *Ibid.* **1958**, *80*, 4220. (b) Carr, R. W.; Walters, W. D. *J. Phys. Chem.* **1965**, *69*, 1073.

results are again better, as the average errors listed in Table III show.

I. Molecular Geometries. Table XII shows the geometries calculated by AM1 for the 138 molecules used in our extended tests, together with experimental values where available. The agreement with experiment is generally satisfactory.

J. Activation Energies of Some Simple Reactions. While no systematic attempt has yet been made to test the ability of AM1 to predict reaction paths, calculations have been carried out for some simple reactions, most of them ones where MNDO gave activation energies that were much too large. While these errors were formerly thought to be due to the overestimation of repulsions in MNDO, it now appears that they were due largely to selection of a less-than-optimal minimum on the parameter hypersurface; see above. In any case AM1 certainly gives better results, in particular for hydrogen abstraction by radicals from paraffins, olefins, or acetylenes, or for addition of radicals to multiple bonds; see Table XIII. Similar comments apply to reactions involving intramolecular migration of hydrogen. Here, however, the errors in AM1 are also quite large. Problems arise here because the experimental barriers are probably too large, owing to neglect of tunnelling. However, it does appear that the AM1 values, while less than the MNDO ones, are still too large. The other reaction, the conrotatory opening of cyclobutene to butadiene, is interesting in that ab initio models give activation energies that are much too large unless allowance is made for electron correlation.²⁶ The

AM1 value compares quite well with that (35.8 kcal/mol) from a recent "state-of-the-art" calculation by Schaefer et al.²⁷

Conclusions

As the tests reported here indicate, AM1 seems to represent a very real improvement over MNDO, with no increase in the computing time needed. The specific failings in MNDO have been at least moderated while the average error for molecules of other kinds has also been reduced. The main gains are the ability of AM1 to reproduce hydrogen bonds and the promise of better estimates of activation energies for reactions. We hope soon to have AM1 parameters available for the other elements already parameterized in MNDO.

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Registry No. C, 7440-44-0; H atom, 12385-13-6; O atom, 17778-80-2; N atom, 17778-88-0.

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