O-H are used in the MINDO method, too.
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(44) (a) M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, submitted; (b) M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, to be published.
(45) D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 37** (1971).
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(47) K. R. Roby, *Chem. Phys. Lett.*, **11**, 6, (1971); **12**, 579 (1972).
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Ground States of Molecules. 39. MNDO Results for Molecules Containing Hydrogen, Carbon, Nitrogen, and Oxygen

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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 polycyclic 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]

		$\Delta(\Delta H_f)$, kcal/mol	
Class of compd	No.	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.

Table II. Heats of Formation ΔH_f for Closed Shell Molecules

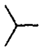
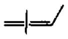
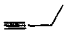
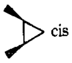
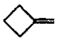
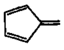
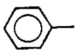
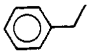
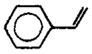
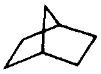
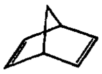
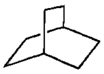
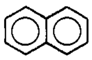
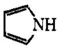
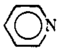
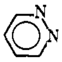
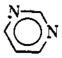
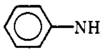
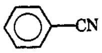
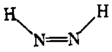
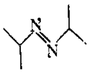
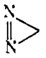
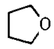
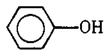
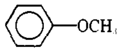
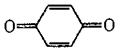
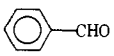
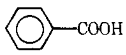
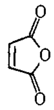
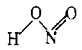
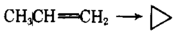
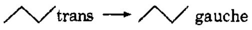
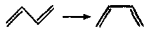
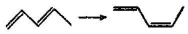
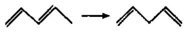
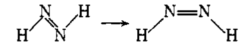
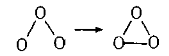
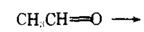
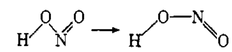
	ΔH_f, kcal/mol			
Molecule	Calcd	Exptl	Error	Ref
H_2	0.7	0.0	+0.7	
CH4	−11.9	−17.9	+6.0	*a*
C_2H_6	−19.7	−20.2	+0.5	*a*
C_2H_4	15.3	12.5	+2.8	*a*
C_2H_2	57.3	54.3	+3.0	*a*
$CH_3CH_2CH_3$	−24.9	−24.8	−0.1	*a*
$CH_3CH{=}CH_2$	4.9	4.9	0.0	*a*
$CH_3C{\equiv}CH$	40.9	44.4	−3.5	*a*
$CH_2{=}C{=}CH_2$	43.8	45.6	−1.8	*a*
	−29.7	−30.4	+0.7	*a*
	−26.8	−32.4	+5.6	*a*
	0.3	−0.2	+0.5	*a*
	−5.1	−3.0	−2.1	*a*
	−4.0	−1.9	−2.1	*a*
	−2.1	−4.3	+2.2	*a*
	33.4	38.8	−5.4	*a*
	28.9	26.0	+2.9	*a*
	35.6	39.5	−3.9	*a*
	24.4	34.7	−10.3	*a*
	65.0	72.8	−7.8	*b*
	102.2	113.0	−10.8	*b*
	−34.4	−35.1	+0.7	*a*
	−24.6	−40.3	+15.7	*a*
	18.7	18.1	+0.6	*a*
	20.0	19.1	+0.9	*a*
	25.9	25.3	+0.6	*a*
	11.2	12.7	−1.5	*a*
	−1.8	1.3	−3.1	*c*
	68.2	66.2	+2.0	*a*
	53.6	58.2	−4.6	*a*
	39.1	46.4	−7.3	*c*
	37.8	47.9	−10.1	*a*
	−11.9	6.8	−18.7	*a*
	31.0	37.5	−6.5	*c*
	6.4	19.8	−13.4	*c*
	10.9	29.1	−18.2	*d*
	−30.5	−18.4	−12.1	*a*
	−0.4	8.2	−8.6	*a*
	32.0	31.9	+0.1	*a*
	53.6	47.5	+6.1	*a*
	−34.8	−29.5	−5.3	*a*
	−10.0	−1.1	−8.9	*a*
	14.4	25.4	−11.0	*a*
	21.2	19.8	+1.4	*a*
	13.5	12.0	+1.5	*a*
	8.6	7.2	+1.4	*a*
	37.5	35.3	+2.2	*a*
	33.6	43.9	−10.3	*a*
	69.1	51.9	+17.2	*a*
	33.7	44.3	−10.6	*a*
	28.6	30.9	−2.3	*a*
	30.2	37.3	−7.1	*c*
	−10.3	−12.4	+2.1	*e*
	62.6	59.7	+2.9	*c*
	−26.3	−24.1	−2.2	*e*
	38.1	36.1	+2.0	*a*
Adamantane	−26.4	−31.9	+5.5	*f*
Cubane	99.1	148.7	−49.6	*a*
N_2	8.0	0.0	+8.0	
NH_3	−6.3	−11.0	+4.7	*g*
CH_3NH_2	−7.5	−5.5	−2.0	*a*
$(CH_3)_2NH$	−6.6	−4.4	−2.2	*a*
$(CH_3)_3N$	−2.8	−5.7	+2.9	*a*
$C_2H_5NH_2$	−12.9	−11.4	−1.5	*a*
n-$C_3H_7NH_2$	−17.9	−16.8	−1.1	*a*
i-$C_3H_7NH_2$	−16.0	−20.0	+4.0	*a*
t-$C_3H_7NH_2$	−15.1	−28.9	+13.8	*a*
	25.2	30.2	−5.0	*a*
	32.4	25.9	+6.5	*a*
	28.7	34.6	−5.9	*a*
	44.2	66.5	−22.3	*a*
	35.5	47.0	−11.5	*a*
	38.3	46.9	−8.6	*a*
	22.0	20.8	+1.2	*a*
HCN	34.9	32.3	+2.6	*g*
CH_3CN	18.9	20.9	−2.0	*h*
C_2H_5CN	13.4	12.1	+1.3	*b*
$CH_2{=}CH{-}CN$	43.7	44.1	−0.4	*a*
	74.6	81.3	−6.7	*a*
$NC{-}C{\equiv}C{-}CN$	110.7	126.5	−15.8	*a*
$(CN)_2$	65.9	73.8	−7.9	*a*
	51.8	51.5	+0.3	*a*
CH_3NC	60.0	35.6	+24.4	*h*
$NH_2{-}NH_2$	14.3	22.8	−8.5	*g*
$CH_3NH{-}NH_2$	16.6	22.6	−6.0	*a*
$(CH_3)_2N{-}NH_2$	19.1	20.0	−0.9	*a*
$CH_3NH{-}NHCH_3$	15.8	22.0	−6.2	*a*
	33.8	50.9	−17.1	*g*

Table II (*Continued*)

Molecule	ΔH_f, kcal/mol			Ref
	Calcd	Exptl	Error	
	2.2	8.6	−6.4	*i*
CH_2N_2	67.1	71	−3.9	*j*
	72.5	79	−6.5	*j*
HN_3	73.0	70.3	+2.7	*h*
O_2	12.2	22.0	−9.8	*k, l*
O_3	48.5	34.2	14.3	*g*
H_2O	−60.9	−57.8	−3.1	*g*
CH_3OH	−57.4	−48.1	−9.3	*a*
C_2H_5OH	−63.0	−56.2	−6.8	*a*
n-C_3H_7OH	−67.7	−61.2	−6.5	*a*
i-C_3H_7OH	−65.4	−65.1	−0.3	*a*
t-C_4H_9OH	−64.3	−74.7	+10.4	*a*
CH_3OCH_3	−51.2	−44.0	−7.2	*a*
$C_2H_5OC_2H_5$	−62.0	−60.3	−1.7	*a*
	−15.5	−12.6	−2.9	*a*
	−8.7	−8.3	−0.4	*a*
	−24.7	−23.0	−1.7	*a*
	−18.0	−17.3	−0.7	*a*
HO—OH	−38.2	−32.5	−5.7	*g*
$CH_3O{-}OCH_3$	−28.3	−30.1	+1.8	*a*
$C_2H_5O{-}OC_2H_5$	−39.1	−46.1	+7.0	*a*
CO	−6.2	−26.4	+20.2	*a*
CO_2	−75.4	−94.1	+18.7	*a*
C_3O_2	−24.1	−22.4	−1.7	*a*
CH_2O	−33.0	−26.0	−7.0	*a*
CH_3CHO	−42.4	−39.7	−2.7	*a*
C_2H_5CHO	−48.1	−45.5	−2.6	*a*
$(CH_3)_2CO$	−49.5	−51.9	+2.4	*a*
CH_2CO	−7.0	−11.4	+4.4	*m*
$(CHO)_2$	−61.6	−50.7	−10.9	*a*
$(CH_3CO)_2$	−78.9	−78.2	−0.7	*a*
$CH_3COCH_2COCH_3$	−83.3	−90.5	+7.2	*a*
	−33.1	−29.3	−3.8	*a*
	−9.8	−8.8	−1.0	*a*
HCOOH	−92.7	−90.6	−2.1	*a*
CH_3COOH	−101.2	−103.3	+2.1	*a*
C_2H_5COOH	−105.7	−108.4	+2.7	*a*
$(COOH)_2$	−174.3	−175.0	+0.7	*a*
	−65.9	−70.1	+4.2	*a*
$HCOOCH_3$	−85.6	−83.6	−2.0	*b*
CH_3COOCH_3	−93.6	−97.9	+4.3	*b*
$CH_3CO{-}O{-}COCH_3$	−132.8	−137.1	+4.3	*a*
	−88.7	−95.2	+6.5	*a*
$HCONH_2$	−39.8	−44.5	+4.7	*g*
$HCON(CH_3)_2$	−36.9	−45.8	+8.9	*a*
N_2O	30.9	19.6	+11.3	*g*
	−40.6	−18.8	−21.8	*g*
$HONO_2$	−17.5	−32.1	+14.6	*g*
CH_3ONO	−36.6	−15.8	−20.8	*a*
CH_3NO_2	3.3	−17.9	+21.2	*a*

[a] J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970. [b] D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969. [c] R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Am. Chem. Soc.*, 90, 4315 (1968). [d] W. D. Good, R. T. Moore, A. G. Osborn, and D. R. Douslin, *J. Chem. Thermodyn.*, 6, 303 (1974). [e] P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Am. Chem. Soc.*, 92, 3277 (1970). [f] Average value from two determinations: M. Mansson, N. Rapport, and E. F. Westrum, *J. Am. Chem. Soc.*, 92, 7296 (1970); R. S. Butler, A. S. Carson, P. G. Laye, and W. V. Steele, *J. Chem. Thermodyn.* 3, 277 (1971). [g] D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37 (1971). [h] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Baily, and R. H. Schumm, *Natl. Bur. Stand. (U.S.), Tech. Note*, No. 270-3 (1968). [i] P. S. Engel, J. L. Wood, J. A. Sweet, and M. L. Margrave, *J. Am. Chem. Soc.*, 96, 2381 (1974). [j] S. W. Benson, F. R. Cruickshanck, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 69, 279 (1969). [k] Calculated without CI. [l] G. Herzberg, "Spectra of Diatomic Molecules", 2nd ed, Van Nostrand, New York, N.Y., 1950. [m] R. L. Nuttall, A. H. Lauffer, and M. V. Kilday *J. Chem. Thermodyn.*, 3, 167 (1971).

Table III. Heats of Isomerization ΔH_{isom} for Closed Shell Molecules

Isomerization reaction	ΔH_{isom}, kcal/mol		
	Calcd	Exptl[a]	Error
$CH_3C{\equiv}CH \rightarrow CH_2{=}C{=}CH_2$	2.9	1.3	+1.6
	26.3	21.8	+4.5
	6.3	7.8	−1.5
	0.5	0.6[b]	−0.1
	1.1	1.1	0.0
	5.4	2.8	+2.6
	3.0	−1.3	+4.3
	0.5	2.0	−1.5
	1.3	1.0	+0.3
	7.2	7.2	0.0
	9.8	−5.2	+15.0
$C_2H_5NH_2 \rightarrow (CH_3)_2NH$	6.3	7.0	−0.7
	1.8	>0[c]	
$CH_3CN \rightarrow CH_3NC$	41.1	14.7	+26.4
	30.5		
$C_2H_5OH \rightarrow (CH_3)_2O$	11.8	12.2	−0.4
$CH_3CH{=}O \rightarrow CH_2{=}CH{-}OH$	7.5		
	26.9	27.1	−0.2
$CH_3COOH \rightarrow HCOOCH_3$	15.6	19.7	−4.1
	1.6	0.5	−1.1

[a] Unless noted otherwise, the experimental data were derived from Table II. [b] R. A. Bonham and L. S. Bartell, *J. Am. Chem. Soc.*, 81, 3491 (1959). [c] A. Trombetti, *Can. J. Phys.*, 46, 1005 (1968).

Table IV. Rotational Barriers

Molecule	Barrier, kcal/mol			Ref
	Calcd	Exptl	Error	
$CH_2{=}CH_2$	62.5[b]	65.0	−2.5	*a*
$CH_3\text{-}CH_3$	1.0	2.9	−1.9	*c*
$CH_3\text{-}NH_2$	1.1	2.0	−0.9	*d*
$CH_3\text{-}OH$	0.7	1.1	−0.4	*e*
$NH_2\text{-}NH_2$				
Cis	8.0			*f*
Trans	0.0			
HO-OH				
Cis	6.9	7.0	−0.1	*g*
Trans	0.0	1.1	−1.1	

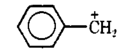
[a] B. S. Rabinovitch and F. S. Looney, *J. Chem. Phys.*, **23**, 2439 (1965). [b] Calculated without CI. [c] S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 962 (1968). [d] D. R. Lide, Jr., *ibid.*, **27**, 343 (1957). [e] E. V. Ivash and D. M. Dennison, *ibid.*, **21**, 1804 (1953). [f] No experimental data. Since the two amino groups are orthogonal to each other in the equilibrium structure, there must be a finite trans barrier. [g] R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, *J. Chem. Phys.*, **42**, 1931 (1965).

Table V. Heats of Formation ΔH_f for Neutral Radicals

Radical	ΔH_f, kcal/mol			Ref
	Calcd	Exptl	Error	
CH_3	25.8	34.8	−9.0	*a*
CH_3CH_2	12.8	25	−12	*b*
$(CH_3)_2CH$	1.5	16.8	−15.3	*b*
$(CH_3)_3C$	−7.2	4.5	−11.7	*b*
Vinyl	63.7	59.6	+4.1	*c*
Allyl	35.3	40	−5	*c*
NH_2	37.1	40.1	−3.0	*a*
CH_3NH	32.9	37	−4	*b*
OH	0.5	9.5	−9.0	*d*
CH_3O	0.1	−0.5	+0.6	*b*
HCO	−0.5	10.4	−10.9	*d*
NO	−0.2	21.6	−21.8	*a*
NO_2	−4.6	7.9	−12.5	*a*
N_3	102.4	99	+3	*d*

[a] See footnote *g* of Table II. [b] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (1969). [c] F. P. Lossing, *Can. J. Chem.*, **49**, 357 (1971). [d] M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud, and L. C. Walker, *J. Phys. Chem. Ref. Data*, **3**, 311 (1974).

Table VI. Heats of Formation ΔH_f for Cations

Cation	,ΔH_f, kcal/mol			Ref
	Calcd	Exptl	Error	
CH_3^+	243.9	260	−16	*a*
$CH_3CH_2^+$	219.7[h]	219	+1	*b*
$(CH_3)_2CH^+$	200.8	192	+9	*c*
$(CH_3)_3C^+$	187.3	176	+11	*b*
$CH_2{=}CH^+$	265.5[h]	266	0	*d*
	221.3	226	−5	*d*
	207.5	209	−1	*b*
	217.9	216	+2	*b*
NH_4^+	165.0	155	+10	*e*
$CH_2{=}NH_2^+$	186.9	178	+9	*b*
H_3O^+	134.2	139	−5	*f*
HCO^+	184.6	199	−14	*a*
$CH_2{=}O^+H$	155.5	167	−11	*g*
NO^+	230.5	237	−6	*f*
NO_2^+	240.5	233	+8	*b*

[a] See footnote *d* of Table V. [b] See footnote *b* of Table V. [c] S. L. Chong and J. L. Franklin, *J. Am. Chem. Soc.*, 94, 6347 (1972). [d] See footnote *c* of Table V. [e] P. Kebarle, R. Tamdagni, H. Kirooka, and T. B. McMahon, *Int. J. Mass Spectrom. Ion Phys.*, 19, 71 (1976). [f] See footnote *g* of Table II. [g] J. Vogt and J. L. Beauchamp, *J. Am. Chem. Soc.*, 97, 6682 (1975). [h] Value for the classical cation which is predicted to be more stable than the nonclassical one.

Table VII. Mean Absolute Errors for Optimized Bond Lengths and Bond Angles[a]

Geometrical variable	No.	Mean absolute error	
		MNDO	MINDO/3
All bond lengths, Å	228	0.014	0.022
$\rightarrow$C—H, Å	25	0.012	0.017
$=\overset{|}{C}$—H, Å	25	0.006	0.021
≡C—H, Å	6	0.006	0.019
All CH, Å	56	0.009	0.019
C—C, Å	58	0.012	0.019
C=C, Å	31	0.012	0.014
C≡C, Å	7	0.009	0.002
All CC, Å	96	0.012	0.016
NH, Å	9	0.006	0.019
N—C, Å	8	0.008	0.051
N≡C, Å	6	0.008	0.004
All NC, Å	17	0.010	0.029
NN, Å	9	0.032	0.074
OH, Å	7	0.011	0.010
O—C, Å	8	0.016	0.047
O=C, Å	14	0.017	0.012
All OC, Å	22	0.016	0.025
ON, Å	8	0.026	0.026
OO, Å	3	0.117	0.043
All bond angles,[b] deg	91	2.8	5.6
HCH, deg	15	3.1	6.1
HCC, deg	23	1.3	2.6
CCC,[b] deg	12	2.0	5.9
All angles at C,[b] deg	62	2.0	4.4
All angles at N,[b] deg	15	3.2	7.1
All angles at O,[b] deg	9	8.5	10.7
Angles between planes in bicyclic compounds, deg	5	1.6	5.9

[a] Based on the results in Table VIII. [b] Bond angles in rings are not included since they are mainly determined by the topology of the ring. The errors for these angles are considerably smaller than those given in the table.

MNDO approximations since they appeared throughout during our parametrization studies for every combination of parametric functions investigated.[1] As for the third shortcoming (NO bonds), it should be remembered that no molecules with NO bonds were used during the parametrization.[1] It is possible that the errors might have been reduced by a reparametrization, including such compounds in the basis set. Since, however, there was no guarantee that this would be the case and since the errors were not at all excessive, we did not feel that the considerable cost of the reparametrization would be justified.

Even in these three areas the errors in the MNDO heats of formation remain within bounds. The only compound for which the MNDO error exceeds 25 kcal/mol is cubane (error, −49.6 kcal/mol), a compound containing six fused four-membered rings. It is amusing to note that MINDO/3 gave a much better result in this case (error, −8.9 kcal/mol[2]). Since cubane is a "globular" molecule, and since MINDO/3 gives heats of formation that are too positive in such cases, this tendency presumably balanced the equal tendency to give too negative heats of formation for compounds containing four-membered rings. In MNDO the former tendency is corrected, but not the latter, so the calculated heat of formation is much too negative.

Table VIII. Molecular Geometries

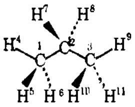
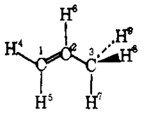
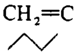
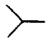
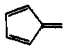
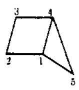
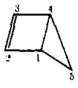
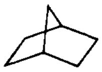
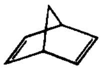
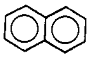
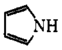
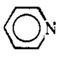
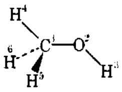
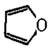
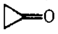
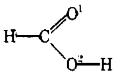
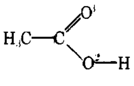
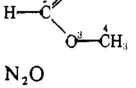
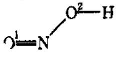
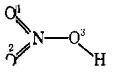
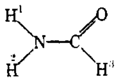
Molecule	Point group	Calcd (obsd) values for geometrical variables[a]	Ref
H_2	$D_{\infty h}$	HH 0.663 (0.742)	*b*
CH_4	T_d	CH 1.104 (1.094)	*c*
C_2H_6	D_{3d}	CC 1.521 (1.536), CH 1.109 (1.091), HCC 111.2 (110.9)	*c*
C_2H_4	D_{2h}	CC 1.335 (1.339), CH 1.089 (1.086), HCC 123.2 (121.2)	*c*
C_2H_2	$D_{\infty h}$	CC 1.194 (1.203), CH 1.051 (1.060)	*c*
	C_{2v}	CC 1.530 (1.526), C^1H^4 1.110 (1.089), C^1H^5 1.109 (1.094), C^2H^7 1.115 (1.096), $C^1C^2C^3$ 115.4 (112.4), $H^7C^2H^8$ 106.0 (106.1), $H^4C^1C^2$ 110.3 (111.8), $H^5C^1H^6$ 107.9 (107.3), C^2–$C^1H^5H^6$ 129.0 (126.4)	*d*
	C_s	C^1C^2 1.340 (1.336), C^2C^3 1.496 (1.501), C^1H^4 1.089 (1.081), C^1H^5 1.089 (1.091), C^2H^6 1.096 (1.090), C^3H^7 1.109 (1.085), C^3H^8 1.111 (1.098), $C^1C^2C^3$ 126.9 (124.3), $H^4C^1C^2$ 122.4 (121.5), $H^5C^1C^2$ 124.3 (120.5), $H^6C^2C^1$ 119.3 (119.0), $H^7C^3C^2$ 113.1 (111.2), $H^8C^3H^9$ 107.7 (106.2), C^2–$C^3H^8H^9$ 126.1 (126.0)	*e*
CH≡C–CH_3	C_{3v}	C^1C^2 1.196 (1.206), C^2C^3 1.445 (1.459), C^1H 1.050 (1.056), C^3H 1.111 (1.105), C^2C^3H 111.0 (110.2)	*f*
CH_2=C=CH_2	D_{2d}	CC 1.306 (1.308), CH 1.090 (1.087), HCH 114.2 (118.2)	*g*
	C_2	C^1C^2 1.531 (1.533), C^2C^3 1.539 (1.533), $C^1C^2C^3$ 114.8 (112.8)	*h*
	C_{3v}	CC 1.541 (1.525), CCC 112.3 (111.2)	*i*
	C_{2h}	C^1C^2 1.497 (1.508), C^2C^3 1.346 (1.347), $C^1C^2C^3$ 126.3 (123.8)	*j*
	C_{2v}	C^1C^2 1.348 (1.330), C^2C^3 1.508 (1.507), $C^1C^2C^3$ 121.9 (122.4)	*k*
	C_{2h}	C^1C^2 1.344 (1.341), C^2C^3 1.465 (1.463), $C^1C^2C^3$ 125.7 (123.3)	*l*
CH_3C≡CCH_3	D_{3d}	C^1C^2 1.444 (1.467), C^2C^3 1.199 (1.213), C^1H 1.111 (1.115), HC^1C^2 111.0 (110.7)	*m*
CH≡C–CH=CH_2	C_s	C^1C^2 1.198 (1.208), C^2C^3 1.417 (1.431), C^3C^4 1.345 (1.341), $C^2C^3C^4$ 125.3 (123.1)	*m*
CH≡C–C≡CH	$D_{\infty h}$	C^1C^2 1.199 (1.205), C^2C^3 1.368 (1.376), C^1H 1.051 (1.046)	*n*
CH_2=C=C=CH_2	D_{2h}	C^1C^2 1.310 (1.318), C^2C^3 1.270 (1.283), C^1H 1.090 (1.083)	*o*
$C(CH_3)_4$	T_d	CC 1.554 (1.539), CH 1.109 (1.120), HCC 111.7 (110.0)	*p*
	D_{3h}	CC 1.525 (1.510), CH 1.096 (1.089), HCH 110.8 (115.1)	*q*
	C_{2v}	C^1C^2 1.328 (1.296), C^2C^3 1.512 (1.509), C^1H 1.062 (1.072), C^3H 1.097 (1.088), HC^1C^2 151.6 (149.9), HC^3H 111.0 (114.6)	*r*
	D_{2d}	CC 1.549 (1.548), CH 1.105 (1.133), HCH 107.6 (108.1), $C^1C^2C^4C^3$ 180.0 (153.0)	*s*
	C_{2v}	C^1C^2 1.355 (1.342), C^2C^3 1.525 (1.517), C^3C^4 1.568 (1.566), C^1H 1.075 (1.083), C^3H 1.104 (1.094), HC^1C^2 135.8 (133.5), HC^3H 108.4 (109.2), C^1–C^4H_2 136.8 (135.8)	*t*
	C_s	CC 1.542 (1.546), CH 1.111 (1.114), HCC 110.7 (111.7)	*u, v*
	C_{2v}	C^1C^2 1.362 (1.342), C^2C^3 1.477 (1.469), C^1C^5 1.521 (1.509)	*w*
	C_{2v}	C^1C^2 1.491 (1.470), C^2C^3 1.366 (1.355), C^3C^4 1.477 (1.476), C^1C^6 1.345 (1.349)	*x*
	D_{3d}	CC 1.539 (1.536), CH 1.114 (1.121), CCC 114.1 (111.4), HCH 105.7 (107.5), CCCC 46.3 (54.9)	*y*
	C_2	C^1C^2 1.346 (1.335), C^2C^3 1.504 (1.504), C^3C^4 1.541 (1.515), C^4C^5 1.539 (1.550), $C^1C^2C^4C^5$ 21.8 (28.3)	*z*
	D_{6h}	CC 1.407 (1.397), CH 1.090 (1.084)	*c*
	C_{2v}	C^1C^2 1.526 (1.498), C^1C^3 1.537 (1.497), C^1H 1.074 (1.071), C^2H_{eq} 1.098 (1.093), C^2H_{ax} 1.097 (1.093), $C^2C^3C^1C^4$ 122.7 (121.7)	*aa*
	D_{2d}	C^1C^2 1.509 (1.469), C^2C^3 1.529 (1.519), C^2H 1.096 (1.091), HC^2H 111.0 (118.4), C^3–C^2H_2 150.6 (148.3)	*bb*
	C_s	C^1C^2 1.540 (1.528), C^2C^3 1.563 (1.565), C^1C^4 1.555 (1.536), C^1C^5 1.530 (1.507), $C^5C^4C^1C^2$ 117.4 (116.7)	*cc*
	C_s	C^1C^2 1.524 (1.511), C^2C^3 1.361 (1.341), C^1C^4 1.567 (1.543), C^1C^5 1.534 (1.533), $C^5C^4C^1C^2$ 117.6 (114.5)	*dd*
	C_{2v}	C^1C^2 1.561 (1.539), C^2C^3 1.557 (1.557), C^1C^7 1.562 (1.560), $C^1C^7C^4$ 93.2 (93.1), $C^6C^1C^4C^3$ 114.2 (113.1)	*ee*
	C_{2v}	C^1C^2 1.540 (1.535), C^2C^3 1.358 (1.343), C^1C^7 1.579 (1.573), $C^1C^7C^4$ 91.7 (94.1), $C^6C^1C^4C^3$ 113.4 (115.6)	*ee*
	D_{2h}	C^1C^2 1.382 (1.364), C^2C^3 1.429 (1.415), C^1C^9 1.439 (1.421), C^9C^{10} 1.435 (1.418)	*ff*
N_2	$D_{\infty h}$	NN 1.103 (1.094)	*b*
NH_3	C_{3v}	NH 1.007 (1.012), HNH 105.3 (106.7)	*c*
CH_3NH_2	C_s	CN 1.460 (1.474), NH 1.008 (1.011), HNC 109.8 (112.0), HNH 105.6 (105.9)	*gg*

Table VIII (*Continued*)

Molecule	Point group	Calcd (obsd) values for geometrical variables[a]	Ref
$(CH_3)_2NH$	C_s	CN 1.462 (1.462), NH 1.009 (1.019), CNC 117.6 (112.2), HNC 109.5 (108.9), H–NCC 130.1 (125.4)	*hh*
$(CH_3)_3N$	C_{3v}	CN 1.464 (1.451), CNC 116.0 (110.9)	*ii*
	C_s	CN 1.479 (1.475), CC 1.516 (1.481), NH 1.008 (1.016), H–NCC 117.9 (112.5)	*jj*
	C_{2v}	N^1C^2 1.398 (1.370), C^2C^3 1.394 (1.382), C^3C^4 1.437 (1.417), N^1H 0.993 (0.996), C^2H 1.082 (1.076), C^3H 1.080 (1.077), HC^2C^3 131.2 (130.8), HC^3C^2 126.5 (125.5)	*kk*
	C_{2v}	N^1C^2 1.353 (1.338), C^2C^3 1.411 (1.394), C^3C^4 1.405 (1.392), C^2H 1.095 (1.086), C^3H 1.089 (1.082), C^4H 1.090 (1.081), $C^6N^1C^2$ 118.2 (116.9), $N^1C^2C^3$ 122.8 (123.8), $C^2C^3C^4$ 118.8 (118.5), $C^3C^4C^5$ 118.6 (118.4), HC^2C^3 121.3 (120.2), HC^3C^2 120.3 (120.1)	*ll*
HCN	$C_{\infty v}$	CN 1.160 (1.154), CH 1.055 (1.063)	*f*
CH_3CN	C_{3v}	CN 1.162 (1.157), CC 1.451 (1.458), CH 1.110 (1.104), HCC 110.6 (109.5)	*f*
$CH_2{=}CH{-}CN$	C_s	C^1C^2 1.344 (1.339), C^2C^3 1.423 (1.426), C^3N 1.162 (1.164), $C^1C^2C^3$ 124.9 (122.6)	*mm*
$CH{\equiv}C{-}CN$	$C_{\infty v}$	C^1C^2 1.197 (1.205), C^2C^3 1.372 (1.378), C^3N 1.163 (1.159), C^1H 1.052 (1.057)	*f*
$(CN)_2$	$D_{\infty h}$	CN 1.161 (1.154), CC 1.377 (1.389)	*c*
CH_3NC	C_{3v}	C^1N^2 1.424 (1.424), N^2C^3 1.191 (1.166), C^1H 1.114 (1.101), HC^1N^2 110.2 (109.1)	*f*
H_2NNH_2	C_2	NN 1.397 (1.449), NH 1.021 (1.022), HNN 107.2 (112.0), HNH 103.1 (106.0), HNNH 180.0 (90.0)	*nn, oo*
$CH_3N{=}NCH_3$, trans	C_{2h}	CN 1.474 (1.474), NN 1.222 (1.254), CNN 116.9 (111.9)	*pp*
CH_2N_2	C_{2v}	CN 1.310 (1.32), NN 1.141 (1.12), CH 1.086 (1.08), HCH 120.7 (127)	*c*
CH_3N_3	C_s	C^1N^2 1.460 (1.468), N^2N^3 1.253 (1.216), N^3N^4 1.130 (1.130), $C^1N^2N^3$ 119.1 (116.8), $N^2N^3N^4$ 164.9 (180.0 assumed)	*qq*
O_2	$D_{\infty h}$	OO 1.135 (1.216)	*b*
O_3	C_{2v}	OO 1.191 (1.278), OOO 117.6 (116.8)	*c*
H_2O	C_{2v}	OH 0.943 (0.957), HOH 106.8 (104.5)	*c*
H_2O_2	C_2	OO 1.295 (1.475), OH 0.961 (0.950), HOO 107.3 (94.8), HOOH 180.0 (119.8)	*rr, ss*
	C_s	$C^1O^2$1.391 (1.425), O^2H^3 0.946 (0.945), C^1H^4 1.115 (1.094), C^1H^5 1.119 (1.094), $C^1O^2H^3$ 111.6 (108.5), $H^4C^1O^2$ 108.1 (107.0), $H^5C^1H^6$ 107.4 (108.6), O^2–$C^1H^5H^6$ 129.9 (129.8)	*tt*
$(CH_3)_2O$	C_{2v}	CO 1.396 (1.410), COC 120.0 (111.7)	*uu*
	C_{2v}	CO 1.417 (1.435), CC 1.513 (1.470), CH 1.102 (1.084), HCH 111.7 (116.3), C–CH_2 159.2 (158.1)	*vv*
	C_{2v}	O^1C^2 1.367 (1.362), C^2C^3 1.390 (1.361), C^3C^4 1.444 (1.431), C^2H 1.084 (1.075), C^3H 1.079 (1.077), HC^2O^1 117.1 (115.9), HC^3C^4 126.6 (128.0)	*ww*
CO	$C_{\infty v}$	CO 1.163 (1.128)	*b*
CO_2	$D_{\infty h}$	CO 1.186 (1.162)	*c*
$CH_2{=}O$	C_{2v}	CO 1.216 (1.208), CH 1.106 (1.116), HCH 113.0 (116.5)	*xx*
$CH_3{-}CH{=}O$	C_s	C^1C^2 1.517 (1.501), C^2O 1.221 (1.216), C^2H 1.112 (1.114), C^1C^2O 125.0 (123.9), C^1C^2H 114.0 (117.5)	*yy*
$(CH_3)_2CO$	C_{2v}	CC 1.527 (1.507), CO 1.227 (1.222), CCC 117.2 (117.2)	*zz*
	C_{2v}	C^1O 1.203 (1.191), C^1C^2 1.500 (1.475), C^2C^3 1.550 (1.575)	*aaa*
CH_2CO	C_{2v}	C^1C^2 1.319 (1.314), C^2O 1.184 (1.161), C^1H 1.085 (1.083), HC^1H 116.5 (122.6)	*bbb*
$CH_2{=}CH{-}CH{=}O$	C_s	C^1C^2 1.342 (1.345), C^2C^3 1.488 (1.470), C^3O 1.223 (1.219), C^3H 1.111 (1.108), $C^1C^2C^3$ 124.9 (119.8), C^2C^3O 123.8 (123.2), C^2C^3 H 115.6 (115.1)	*ccc*
$CH{\equiv}C{-}CH{=}O$	C_s	C^1C^2 1.197 (1.209), C^2C^3 1.439 (1.445), C^3O 1.222 (1.215), C^1H 1.052 (1.055), C^3H 1.111 (1.106), $C^1C^2C^3$ 178.9 (178.4), C^2C^3O 124.1 (123.6), C^2C^3H 114.0 (113.9)	*ddd*
$(CHO)_2$, trans	C_{2h}	CO 1.220 (1.207), CC 1.529 (1.525), CH 1.108 (1.116), OCC 122.0 (121.2), HCC 116.0 (112.2)	*l*
	C_s	CO^1 1.227 (1.202), CO^2 1.354 (1.343), O^2H 0.949 (0.972), CH 1.105 (1.097), O^1CO^2 120.6 (124.9), CO^2H 116.3 (106.3), HCO^1 126.7 (124.1)	*eee*
	C_s	CC 1.522 (1.520), CO^1 1.231 (1.214), CO^2 1.359 (1.364), O^2H 0.949 (0.97), CCO^1 126.8 (126.6), CCO^2 114.5 (110.6), CO^2H 115.6 (107.0)	*fff*
	C_s	O^1C^2 1.224 (1.200), C^2O^3 1.356 (1.334), O^3C^4 1.404 (1.437), $O^1C^2O^3$ 122.2 (125.9), $C^2O^3C^4$ 125.7 (114.8)	*ggg*
N_2O	$C_{\infty v}$	NN 1.127 (1.126), NO 1.181 (1.186)	*f*
N_2O_4	D_{2h}	NN 1.632 (1.750), NO 1.189 (1.180), ONO 128.8 (133.7)	*hhh*
	C_s	NO^1 1.166 (1.163), NO^2 1.312 (1.433), O^2H 0.958 (0.954), O^1NO^2 113.3 (110.7), NO^2H 110.0 (102.1)	*iii*
	C_s	NO^1 1.202 (1.199), NO^2 1.211 (1.211), NO^3 1.340 (1.406), O^3H 0.962 (0.964), O^1NO^2 115.1 (113.9), O^2NO^3 118.4 (115.9), NO^3H 114.1 (102.2)	*jjj*
	C_1	CN 1.408 (1.376), CO 1.225 (1.193), CH^3 1.108 (1.102), NH^1 1.001 (1.014), NH^2 1.000 (1.002), H^1NCO 17.0 (7 ± 5), H^2NCH^3 −28.1 (−12 ± 5)	*kkk*
$H_2N{-}NO_2$	C_s	NN 1.407 (1.427), NO 1.209 (1.206), NH 1.018 (1.005), ONO 124.2 (130.1), HNN 112.2 (115.2), N–NH_2 129.9 (128.2)	*lll*

[a] Bond length A^iB^j (in Å), bond angle $A^iB^jC^k$ (in deg), and dihedral angle $A^iB^jC^kD^l$ (in deg) of A–B with respect to C–D measured counter-

Table VIII (*Continued*)

clockwise along B–C, and angle A^i–$B^jC^kD^l$ (in deg) of A–B with the plane BCD. The superscripts *i, j, k, l* number the atoms in the molecule according to IUPAC rules; they are left out when the atoms can be specified unambiguously without them. [b] G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules", 2nd ed, Van Nostrand, New York, N.Y., 1950. [c] G. Herzberg, "Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand, New York, N.Y., 1966. [d] D. R. Lide, Jr., *J. Chem. Phys.*, 33, 1514 (1960). [e] D. R. Lide, Jr., and D. Christensen, *ibid.*, 35, 1374 (1961). [f] C. C. Costain, *ibid.*, 29, 864 (1958). [g] A. G. Maki and R. A. Toth, *J. Mol. Spectrosc.*, 17, 136 (1965). [h] R. A. Bonham and L. S. Bartell, *J. Am. Chem. Soc.*, 81, 3491 (1959). [i] D. R. Lide, Jr., *J. Chem. Phys.*, 33, 1519 (1960). [j] A. Almenningen, I. M. Anfinsen, and A. Haaland, *Acta Chem. 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Lees and J. G. Baker, *ibid.*, 48, 5299 (1968). [uu] U. Blukis, P. H. Kasai, and R. J. Myers, *ibid.*, 38, 2753 (1963). [vv] T. E. Turner and J. A. Howe, *ibid.*, 24, 924 (1956). [ww] B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaard, J. Rastrup-Andersen, and M. Schottländer, *J. Mol. Spectrosc.*, 9, 124 (1962). [xx] K. Takagi and T. Oka, *J. Phys. Soc. Jpn.*, 18, 1174 (1963). [yy] R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *J. Chem. Phys.*, 26, 1695 (1957). [zz] R. Nelson and L. Pierce, *J. Mol. Spectrosc.*, 18, 344 (1965). [aaa] J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Am. Chem. Soc.*, 91, 1896 (1969). [bbb] A. P. Cox, L. F. Thomas, and J. Sheridan, *Spectrochim. Acta*, 15, 542 (1959). [ccc] E. A. Cherniak and C. C. Costain, *J. Chem. Phys.*, 45, 104 (1966). [ddd] C. C. Costain and J. R. Morton, *ibid.*, 31, 389 (1959). [eee] G. H. Kwei and R. F. Curl, Jr., *ibid.*, 32, 1592 (1960). [fff] J. L. Derissen, *J. Mol. Struct.*, 7, 67 (1971). [ggg] R. F. Curl, Jr., *J. Chem. Phys.*, 30, 1529 (1959). [hhh] D. W. Smith and K. Hedberg, *J. Chem. Phys.*, 25, 1282 (1956). [iii] D. J. Finnigan, A. P. Cox, A. H. Brittain, and J. G. Smith, *J. Chem. Soc., Faraday Trans. 2*, 68, 548 (1972). [jjj] A. P. Cox and J. M. Riveros, *J. Chem. Phys.*, 42, 3106 (1965). [kkk] C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, 32, 158 (1960). [lll] J. K. Tyler, *J. Mol. Spectrosc.*, 11, 39 (1963).

The relative energies of pairs of isomers are generally well reproduced by MNDO; see Table III. The only serious discrepancy occurs in the comparison *n*-pentane/neopentane, where MNDO predicts the latter to be much less stable. This of course is due to the tendency of MNDO to give heats of formation for crowded molecules that are too positive. The error here is, however, less than it was in MINDO/3 (ΔH_{isom}(calcd), 24.5 kcal/mol).

Rotational barriers (see Table IV) are predicted only moderately well by MNDO. As in MINDO/3, the calculated barrier for ethane is about one-third of the experimental value. For hydrazine and hydrogen peroxide, MNDO fails to reproduce the trans barriers, although the difference in energy between the trans and cis conformations is quite well reproduced. In the case of hydrogen peroxide, it is not surprising that no trans barrier is predicted since the inclusion of polarization functions in the basis set is found essential to obtain a barrier.[4] For hydrazine, the MNDO torsional potential shows a shoulder at 90° but no local minimum; we have to conclude that the tendency of the lone pairs to be orthogonal to each other (which is responsible for the skew structure of hydrazine[5]) is underestimated in MNDO.

Table V lists MNDO heats of formation for neutral radicals, calculated by the half-electron approximation,[6,7] while Table VI gives MNDO heats of formation for some closed shell cations. The mean absolute errors for radicals (8.7 kcal/mol) and for cations (7.2 kcal/mol) are slightly higher than for neutral molecules (6.3 kcal/mol) but of the same order of magnitude. The radicals systematically tend to be predicted somewhat too stable, whereas there is no such trend for the cations.

(III) Molecular Geometries

Table VII compares MNDO and MINDO/3 results for bond lengths and bond angles. Table VIII shows the optimized MNDO structures for 80 molecules, along with the experimental data. Full structures are given for small molecules, but as a rule only the molecular skeletons are given for larger ones. When comparing calculated and observed values for geometrical variables, it should be remembered that the experimental r_s values from microwave spectroscopy and r_g values from electron diffraction differ somewhat from the equilibrium r_e values. Discrepancies of less than 0.01 Å in bond lengths and 1° in angles are therefore not too meaningful.

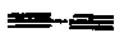
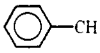
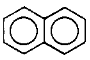
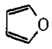
The mean absolute error in bond lengths (see Table VII) is reduced from 0.022 Å in MINDO/3 to 0.014 Å in MNDO. Major improvements are found for CH, NH, NN, N-C, and O-C bonds, whereas MINDO/3 is superior for OO bond lengths, for which the MNDO values are much too small. This failure of MNDO is related to the use of atomic parameters.

Table IX. Mean Absolute Errors ΔIP_1 for First Ionization Potentials[a]

Class of compd	No.	ΔIP, eV MNDO	ΔIP, eV MINDO/3
All compounds	51	0.48	0.71
Hydrocarbons	22	0.41	0.31
Nitrogen compounds (CHN)	13	0.54	1.58
Oxygen compounds (CHO)	16	0.53	0.56

[a] Based on the results in Table X.

Table X. First Ionization Potentials IP_1

Molecule	IP, eV Calcd[a]	IP, eV Exptl[b]	Error	Ref
H_2	15.74	15.98	−0.24	*c*
CH_4	13.87	14.0[d]	−0.13	*c*
C_2H_6	12.70	12.1	+0.6	*c*
C_2H_4	10.18	10.51	−0.33	*c*
C_2H_2	11.03	11.40	−0.37	*c*
$CH_3CH_2CH_3$	12.34	11.5	+0.8	*e*
$CH_3CH{=}CH_2$	9.97	9.88	+0.11	*f*
$CH_3C{\equiv}CH$	10.73	10.37	+0.36	*c*
$CH_2{=}C{=}CH_2$	10.02	10.07	−0.05	*g*
	9.14	9.08	+0.06	*c*
	10.00	10.17	−0.17	*c*
	12.12	11.4	+0.7	*e*
	12.12	11.3[d]	+0.8	*e*
	11.43	11.0[d]	+0.4	*c*
	9.89	9.86	+0.03	*h*
	11.81	11.0[d]	+0.8	*i*
	9.77	9.43	+0.34	*h*
	9.72	9.18	+0.54	*h*
	9.04	8.57	+0.47	*j*
	9.39	9.25	+0.14	*c*
 CH3	9.28	8.82	+0.46	*c*
	8.57	8.15	+0.42	*c*
N_2	14.88	15.60	−0.72	*c*
NH_3	11.19	10.85	+0.34	*c*
CH_3NH_2	10.55	9.45	+1.10	*k*
$(CH_3)_2NH$	10.04	8.93	+1.11	*k*
$(CH_3)_3N$	9.59	8.54	+1.05	*k*
	10.68	9.8	+0.9	*c*
	8.57	8.21	+0.36	*j*
	9.69	9.67	+0.02	*l*
HCN	13.42	13.60	−0.18	*c*
CH_3CN	12.80	12.21	+0.59	*c*
$CH_2{=}CH{-}CN$	10.62	10.91	−0.29	*m*
$CH{\equiv}C{-}CN$	11.36	11.60	−0.24	*c*
$(CN)_2$	13.22	13.36	−0.14	*c*
O_3	12.71	12.75	−0.04	*n*
H_2O	12.19	12.62	−0.43	*c*
CH_3OH	11.41	10.96	+0.45	*o*
$(CH_3)_2O$	11.04	10.04	+1.00	*p*
	11.49	10.57	+0.92	*c*
	9.14	8.88	+0.26	*j*
CO	13.43	14.01	−0.58	*c*
CO_2	12.79	13.78	−0.99	*c*
CH_2O	11.04	10.88	+0.16	*c*
CH_3CHO	10.88	10.21	+0.67	*q*
$(CH_3)_2CO$	10.75	9.72	+1.03	*r*
CH_2CO	9.29	9.64	−0.35	*c*
$CH_2{=}CH{-}CHO$	10.69	10.11	+0.58	*c*
$(CHO)_2$	10.75	10.59	+0.16	*c*
HCOOH	11.74	11.51	+0.23	*s*
$HCOOCH_3$	11.61	11.02	+0.59	*t*

[a] Calculated via Koopmans' theorem. [b] Vertical ionization potentials from UV-photoelectron spectroscopy. [c] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970. [d] Band center (average of Jahn–Teller peaks). [e] J. N. Murrell and W. Schmidt, *J. Chem. Soc., Faraday Trans. 2,* 68, 1709 (1972). [f] A. Katrib and J. W. Rabalais, *J. Phys. Chem.*, 77, 2358 (1973). [g] F. Brogli, J. K. Crandall, E. Heilbronner, E. Kloster-Jensen, and S. A. Sojka, *J. Electron Spectrosc. Relat. Phenom.* 2, 455 (1973). [h] P. Bischof and E. Heilbronner, *Helv. Chim. Acta,* 53, 1677 (1970). [i] P. Bischof, E. Haselbach, and E. Heilbronner, *Angew. Chem., Int. Ed. Engl.*, 9, 953 (1970). [j] P. J. Derrick, L. Åsbrink, O. Edquist, B. O. Jonsson, and E. Lindholm, *J. Mass. Spectrom. Ion Phys.*, 6, 161, 177, 191, 203 (1971). [k] J. P. Maier and D. W. Turner, *J. Chem. Soc., Faraday Trans. 2,* 69, 521 (1973). [l] See ref 11b. [m] R. F. Lake and H. Thompson, *Proc. R. Soc. London, Ser. A,* 317, 187 (1970). [n] C. R. Brundle, *Chem. Phys. Lett.*, 26, 25 (1974). [o] M. B. Robin and N. A. Kuebler, *J. Electron Spectrosc. Relat. Phenom.*, 1, 13 (1972). [p] S. Cradock and R. A. Whiteford, *J. Chem. Soc., Faraday Trans. 2,* 68, 281 (1972). [q] W. C. Tam, D. Yee, and C. E. Brion, *J. Electron Spectrosc. Relat. Phenom.*, 4, 77 (1974). [r] C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Am. Chem. Soc.*, 94, 1451 (1972). [s] C. R. Brundle, D. W. Turner, M. B. Robin, and N. A. Kuebler, *Chem. Phys. Lett.*, 3, 292 (1969). [t] D. A. Sweigart and D. W. Turner, *J. Am. Chem. Soc.*, 94, 5592 (1972).

When bond parameters were used in our MNDO parametrization studies,[1] the OO bond lengths could be reproduced without difficulty.

The mean absolute error in bond angles (see Table VII) is reduced from 5.6° in MINDO/3 to 2.8° in MNDO. HCH angles, CCC angles in acyclic compounds, angles at nitrogen, and flap angles in bicyclic compounds are all predicted more reliably in MNDO than in MINDO/3. Bond angles at oxygen tend to be too large in MNDO and HCH angles slightly too small, although the errors are decreased compared to MINDO/3.

Ring conformations are not reproduced well by either MNDO or MINDO/3. Both methods predict cyclobutane, cyclopentane, and cyclopentene to be essentially planar. Note that ab initio calculations with minimal basis sets also underestimate the puckering in these molecules.[8] Cyclohexane and cyclohexene are predicted to be nonplanar, but the optimized structures are somewhat too flat. MNDO gives stronger puckering than MINDO/3.

Structures of trivalent nitrogen compounds are usually reproduced better by MNDO than by MINDO/3. Dimethylamine, trimethylamine, aniline, cyanamide, and nitramide are pyramidal in MNDO, mostly with structures close to experiment, whereas they are planar, or almost planar, in MINDO/3.

(IV) Ionization Potentials

Calculated and observed ionization potentials are compared in Tables IX-XI. The calculated values are negative orbital energies, i.e., we assume the validity of Koopmans' theorem[9] which neglects the electronic reorganization and the change in correlation energy upon ionization. Apart from a few exceptions, the errors introduced by this approximation (Koopmans' defect[10]) are usually less than 1 eV.

The mean absolute error for the first ionization potential (see Table IX) is reduced from 0.71 eV in MINDO/3 to 0.48 eV in MNDO. The main improvement is for nitrogen-containing compounds. The first ionization potentials in MNDO tend to be slightly larger than the experimental values (see Table X).

For higher ionization potentials (see Table XI), MNDO is clearly superior to MINDO/3. The ordering of the MNDO levels and their splittings agree very satisfactorily with experimental data. The results for N_2 are particularly satisfying because the Hartree-Fock method fails to predict the ionizations even in the right order.[12] The results for unsaturated

Table XI. Higher Ionization Potentials IP

Molecule	IP, eV		Assignment[c]	Ref
	Calcd[a]	Exptl[b]		
CH_4	13.87	14.0[d]	$1t_2$	*e*
	30.61	22.91	$1a_1$	
C_2H_6	12.70		$1e_g$	*f*
		12.1		
	13.33		$2a_{1g}$	
	15.09	15.0	$1e_u$	
	24.81	20.41	$1a_{2u}$	
C_2H_4	10.18	10.51	$1b_{1u}$	*g*
	12.64	12.85	$1b_{1g}$	
	14.61	14.66	$2a_g$	
	15.83	15.87	$1b_{2u}$	
C_2H_2	11.03	11.40	$1\pi_u$	*f*
	15.87	16.36	$2\sigma_g$	
	21.01	18.69	$1\sigma_u$	
	9.39	9.24	$1e_{1g}$	*h*
	12.48	11.49	$2e_{2g}$	
	12.61	12.3	$1a_{2u}$	
	14.45	13.8	$2e_{1u}$	
	15.21	14.7	$1b_{2u}$	
	16.79	15.4	$1b_{1u}$	
	17.53	16.85	$2a_{1g}$	
NH_3	11.19	10.88	$2a_1$	*e*
	16.73	16.0	1e	
	32.98	27.0	$1a_1$	
HCN	13.42	13.60	1π	*f*
	14.26	14.0	3σ	
	21.63	19.95	2σ	
N_2	14.88	15.60	$2\sigma_g$	*f*
	16.22	16.98	$1\pi_u$	
	21.06	18.78	$1\sigma_u$	
H_2O	12.19	12.62	$1b_1$	*e*
	14.47	14.74	$2a_1$	
	19.11	18.51	$1b_2$	
	40.04	32.2	$1a_1$	
CO_2	12.79	13.78	$1\pi_g$	*f*
	17.69	17.59	$1\pi_u$	
	17.81	18.08	$2\sigma_u$	
	21.25	19.40	$2\sigma_g$	
$CH_2{=}O$	11.04	10.88	$2b_2$	*i*
	14.19	14.38	$1b_1$	
	16.30	16.00	$2a_1$	
	16.96	16.78	$1b_2$	

[a] Calculated via Koopmans' theorem. [b] Vertical ionization potentials from UV-photoelectron spectroscopy. [c] The numbering of the MO's refers to a valence basis set. The assignments are taken from the references; MNDO gives identical assignments, in all cases. [d] Band center (average of Jahn–Teller peaks). [e] A. W. Potts and W. C. Price, *Proc. R. Soc. London, Ser. A*, 326, 165, 181 (1972). [f] See footnote *c* of Table X. [g] See footnote *r* of Table X. [h] See ref 11b. [i] A. D. Baker, C. Baker, C. R. Brundle, and D. W. Turner, *J. Mass Spectrom. Ion Phys.*, 1, 285 (1968). New experimental results show that the original assignment ($1b_2$, $2a_1$) of the last two bands has to be reversed, see: S. T. Hood, A. Hamnett, and C. E. Brion, *Chem. Phys. Lett.*, 41, 428 (1976).

systems are also very satisfactory, all the ionizations being predicted in the order observed. Previous semiempirical treatments, including MINDO/3, had given spurious high-lying σ levels. Thus MNDO predicts the four highest levels of naphthalene to be of π type, in agreement with ab initio calculations[11a] and experiment,[11b] whereas MINDO/3 inserted several σ levels between the four highest π MO's. The only shortcoming of MNDO is an overestimation of the ionization energies corresponding to MO's with high 2s coefficients, e.g., $1a_1$ in methane, ammonia, or water. This is undoubtedly due to the neglect of 1s–2s interactions, arising from the use of the core approximation in MNDO. Such interactions will of course have little effect on the total energies of molecules but will affect the orbital energies of MO's derived largely from 2s AO's.

Table XII. Mean Absolute Errors $\Delta\mu$ for Dipole Moments[a]

Class of compd	No.	$\Delta\mu$, D	
		MNDO	MINDO/3
All compounds	57	0.30	0.49
Hydrocarbons	11	0.25	0.26
Nitrogen compounds (CHN)	18	0.41	0.77
Oxygen compounds (CHO)	22	0.19	0.37
Nitrogen-oxygen compounds	6	0.50	0.49

[a] Based on the results in Table XIII.

(V) Dipole Moments and Charge Distributions

Calculated and observed dipole moments are compared in Tables XII and XIII. The mean absolute error for the dipole moments (Table XII) is reduced from 0.49 D in MINDO/3 to 0.30 D in MNDO. The greatest improvements are for systems containing heteroatoms. Dipole moments for unsaturated hydrocarbons are usually predicted too low in MNDO (Table XIII).

Net atomic charges for some simple molecules are listed in Table XIV. The MNDO values are usually similar to the corresponding STO-3G ones,[13] which were calculated using orbital exponents optimized for each molecule. In heterosystems particularly, the charge separation between the carbon and hetero atoms is comparable for MNDO and STO-3G but much larger for MINDO/3. There are, however, a few significant differences.

In saturated hydrocarbons, MNDO yields the polarity C^+–H^- for the C–H bond[14] and STO-3G C^-–H^+, but the net charges are in both cases small. Substitution of a methyl group for a hydrogen atom at a center X makes the net atomic charge of X slightly more negative in MNDO but more positive in STO-3G (cf. the series H_2O, CH_3OH, $(CH_3)_2O$). Again, the effects are small, but of opposite sign. Finally, MNDO seems to underestimate the polarization of π electrons by alkyl substituents, judging by the low values of the dipole moments calculated for unsaturated hydrocarbons.

(VI) Computational Aspects

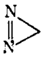
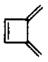
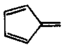
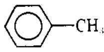
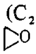
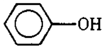
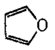
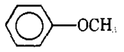
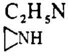
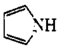
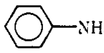
Table XV lists the computation times required for one SCF calculation using various SCF methods. That for a MNDO calculation is only about 20% greater than for a MINDO/3 one. The rate-determining step in both cases is matrix diagonalization, not integral evaluation as in ab initio methods. Derivatives of the energy can therefore be calculated very rapidly in MNDO by finite difference, allowing the use of rapid and efficient procedures for locating minima and transition states on the potential surface for a reaction. The time required for such calculations is also only a little greater than it is for MINDO/3.[15]

Compared with STO-3G, a single SCF calculation with MNDO is faster "only" by a factor of about 20 (see Table XV). Since, however, the calculation of gradients in ab initio procedures is much more time consuming, geometry optimizations will be much faster in MNDO than in STO-3G (estimated factor, 100:1). The computational advantages of MNDO would of course be still more conspicuous in comparisons with more sophisticated ab initio methods.

(VII) Conclusions

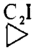
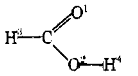
The data and statistics provided in the previous chapters show that the MNDO values for heats of formation, molecular geometries, ionization potentials, and dipole moments are quite close to the experimental values. The MNDO results are superior to the MINDO/3 ones in most respects, particularly for nitrogen-containing compounds. Qualitative improvements

Table XIII. Dipole Moments μ

Molecule	μ, D Calcd.	μ, D Exptl	μ, D Error	Ref	Molecule	μ, D Calcd.	μ, D Exptl	μ, D Error	Ref
$CH_3CH_2CH_3$	0.00	0.08	−0.08	*a*	CH_3NH-NH_2	1.53[g]	1.66[g]	−0.13	*h*
$CH_3CH{=}CH_2$	0.04	0.37	−0.33	*a*	CH_2N_2	1.25	1.50	−0.25	*a*
$CH_3C{\equiv}CH$	0.12	0.78	−0.66	*a*		1.55	1.59	−0.04	*a*
	0.48	0.45	+0.03	*a*	CH_3N_3	1.63	2.17	−0.54	*a*
	0.08	0.13	−0.05	*a*	O_3	1.18	0.53	+0.65	*a*
	0.05	0.20	−0.15	*a*	H_2O	1.78	1.85	−0.07	*a*
	0.18	0.42	−0.24	*a*	CH_3OH	1.48	1.70	−0.22	*a*
	0.22	0.62	−0.40	*b*	C_2H_5OH	1.40	1.69	−0.29	*a*
	0.69	0.42	+0.27	*c*	$(CH_3)_2O$	1.26	1.30	−0.04	*a*
	0.06	0.36	−0.30	*a*	$(C_2H_5)_2O$	1.09	1.15	−0.06	*a*
	0.41	0.68	−0.27	*d*		1.92	1.89	+0.03	*a*
NH_3	1.76	1.47	+0.29	*a*		1.67	1.45	+0.22	*a*
CH_3NH_2	1.48	1.31	+0.17	*a*		0.42	0.66	−0.24	*a*
$(CH_3)_2NH$	1.17	1.03	+0.14	*a*		1.44	1.38	+0.06	*a*
$(CH_3)_3N$	0.75	0.61	+0.14	*a*	CO	0.19	0.11	+0.08	*a*
$C_2H_5NH_2$	1.52	1.22	+0.30	*a*	CH_2O	2.16	2.33	−0.17	*a*
	1.75	1.90	−0.15	*a*	CH_3CHO	2.38	2.69	−0.31	*a*
	1.81	1.74	+0.07	*e*	$(CH_3)_2CO$	2.51	2.88	−0.37	*a*
	1.97	2.22	−0.25	*f*	CH_2CO	1.04	1.42	−0.38	*a*
	1.48	1.53	−0.05	*a*	$CH_2{=}CH-CHO$	2.93	3.12	−0.19	*a*
HCN	2.51	2.98	−0.47	*a*	$CH{\equiv}C-CHO$	2.86	2.47	+0.39	*a*
CH_3CN	2.63	3.92	−1.29	*a*	HCOOH	1.49	1.41	+0.08	*a*
$CH_2{=}CH-CN$	2.97	3.87	−0.90	*a*	CH_3COOH	1.68	1.74	−0.06	*a*
$CH{\equiv}C-CN$	3.21	3.72	−0.51	*a*	C_2H_5COOH	1.64	1.75	−0.11	*a*
CH_3NC	2.17	3.85	−1.68	*a*	$HCOOCH_3$	1.63	1.77	−0.14	*a*
					CH_3COOCH_3	1.74	1.72	+0.02	*a*
					$HCONH_2$	3.09	3.73	−0.64	*a*
					$HCON(CH_3)_2$	3.19	3.82	−0.63	*a*
					N_2O	0.76	0.17	+0.59	*a*
					HONO trans	2.27	1.86	+0.41	*i*
					HONO cis	1.56	1.42	+0.14	*i*
					$HONO_2$	2.78	2.17	+0.61	*a*

[a] R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. **10** (1967) [b] R. D. Brown, F. R. Burden, A. J. Jones, and J. E. Kent, *Chem. Commun.*, 808 (1967). [c] See footnote *x* of Table VIII. [d] M. D. Harmony and K. W. Cox, *J. Am. Chem. Soc.*, 88, 5049 (1966). [e] See footnote *jj* of Table VIII. [f] See footnote *kk* of Table VIII. [g] Inner rotamer. [h] R. P. Lattimer and M. D. Harmony, *J. Chem. Phys.*, 53, 4575 (1970). [i] A. P. Cox, A. H. Brittain, and D. J. Finnigan, *Trans. Faraday Soc.*, 67, 2179 (1971).

Table XIV. Net Atomic Charges q_X[a]

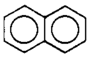
Molecule	Atom X	q_X, |e|	Molecule	Atom X	q_X, |e|
CH_4	C	+0.072	$(CH_3)_2O$	C	+0.196
C_2H_6	C	+0.018		O	−0.335
C_2H_4	C	−0.084	CO	C	+0.184
C_2H_2	C	−0.157	CO_2	C	+0.446
	C	−0.077	CH_2O	C	+0.289
	C	−0.035		O	−0.291
	C	−0.059		C	+0.349
NH_3	N	−0.246		O^1	−0.355
HCN	H	+0.191		O^2	−0.276
	C	−0.090		H^3	+0.081
	N	−0.101		H^4	+0.202
H_2O	O	−0.318	$N^1{=}N^2{=}O$	N^1	−0.062
CH_3OH	C	+0.186		N^2	+0.335
	O	−0.327		O	−0.273

[a] The net atomic charge q_X, in units of the elementary charge |e|, is defined as $q_X = Z_X - \Sigma_\mu{}^X P_{\mu\mu}$, where Z_X is the core charge of atom X, $P_{\mu\mu}$ is a diagonal element of the bond order matrix, and the summation extends over all basis orbitals of atom X.

of MNDO over MINDO/3 are found in cases where directional effects play an important role. These improvements are especially pleasing in view of the facts that MNDO uses considerably fewer adjustable parameters than MINDO/3 and that the computational effort for MNDO is only slightly higher than for MINDO/3.

MNDO therefore seems to represent a significant advance over MINDO/3, especially for compounds containing heteroatoms. Since MINDO/3 has already proved useful in a number of chemical connections,[16] it seems likely that MNDO

Table XV. Computation Times *T* for One SCF Calculation[a]

	T, s			
Molecule	MINDO/3	MNDO	STO-3G[b]	4-31G[b]
CH_4	0.44	0.53	4.60	22.07
C_2H_6	1.65	1.98	26.09	155.91
C_3H_8	3.11	4.21	93.79	
	6.59	7.16	255.56	1759.8
	39.14	48.97	1279.0	

[a] Central processor time on a CDC 6600. The STO-3G and 4-31G programs were provided by Dr. A. Komornicki. [b] On the CDC system, the user is additionally charged for the disk storage of integrals which amounts to about 40% of the total TM charges.

will find numerous applications in the study of reaction mechanisms and other chemical behavior.

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Effect of Electronic State of Carbon Atoms on Their Reactions with Cyclopentadiene in Inert Gas Moderated Systems

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Abstract: Products of the reactions of hot and moderated free carbon atoms with cyclopentadiene have been studied in pure and oxygen scavenged systems. Experiments with different rare gas moderators have provided evidence that both triplet and singlet carbon atoms react with cyclopentadiene and oxygen with comparable efficiencies and many similar products result. In distinction from previous work on oxygen scavenged alkane systems, acetylene is thought to be formed to some extent by thermal or near thermal $C(^3P)$ atoms. The formation of the ring expansion product, benzene, also appears to result in part from $C(^3P)$ reactions. On the other hand, the straight chain C_6H_6 isomers are attributed almost exclusively to singlet atoms.

In the past decade as the result of the application of a variety of techniques,[2] the broad outlines of the chemistry of the free carbon atom have been traced. Insertion into the C–H bond, addition to the π bond, and abstraction of oxygen and halogen atoms have all been identified.[13] While some progress has been made in understanding the effects of excess kinetic energy on carbon atom reactivity, the problem is complex because of the need to sort out the effects of electronic excitation from those due to translational energy. This in turn is complicated by the fact that our knowledge of the differences in the chemistry of the ground $C(^3P)$ and low-lying $C(^1D)$ and $C(^1S)$ states is rudimentary. Some progress in unraveling these problems have been made recently as the result of a series of experiments involving production of C atoms by flash photolysis of C_3O_2 in the presence of simple substrates.[3] The decay of these atoms was followed spectroscopically and rate constants were deduced. This work has shown that the $C(^1D)$ atom reacts efficiently with both methane and ethylene. Acetylene is a major product of the methane reaction in agreement with earlier results of experiments with nucleogenic carbon atoms.[13] The $C(^3P)$ atom appears to react slowly with methane, and there is evidence from microwave discharge experiments with C_3O_2 that its reaction with ethylene is also slow.[6] Such information is of considerable value in the interpretation of more complex systems.

Also of significance is the finding of Peterson[14] that the choice of rare gas used as moderator in the nucleogenic experiments has a marked effect on triplet/singlet atom ratio, which varies from about 0.45 with neon to 2.3 or more with krypton and xenon. Taylor, Ache, and Wolf[15] have also carried out moderation experiments in oxygen scavenged alkane systems. Their results have lead to the proposals that hot $C(^1D)$ forms methyne, hot $C(^3P)$ and thermal $C(^1D)$ lead to acetylene, and thermal $C(^3P)$ reacts 10^4 to 10^6 times faster with