Ground States of σ-Bonded Molecules. X.[1] Extension of the MINDO/2 Method to Compounds Containing Nitrogen and/or Oxygen[2]

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Abstract: The MINDO/2 method[1] has been successfully extended to compounds containing nitrogen and/or oxygen. By including these elements, the degeneracy[1] of solutions for the parameters for carbon and hydrogen has been reduced. The present procedure gives better results for hydrocarbons than the earlier[1] treatment and it also gives generally satisfactory results for compounds containing nitrogen and/or oxygen.

The purpose of the investigations described in this series of papers is to develop a semiempirical SCF MO treatment of organic molecules, including all the valence electrons, that will enable their ground state properties to be calculated with "chemical" accuracy. This objective has already been achieved in the case of conjugated molecules, using the Hückel σ,π approximation together with a treatment[5] of the π electrons based on the Pople method, and earlier papers of the present series[6] described extensions of the method in which all the valence electrons were included in the MO calculations. In these preliminary studies we were unable to estimate heats of formation and molecular geometries simultaneously; we were, however, able to develop procedures which gave good values for the heats of formation if the geometries were calculated using a set of "standard" bond lengths and bond angles.

In the preceding paper,[1] it was shown that this limitation was not inherent in the approximation used, but due rather to the difficulty of optimizing parameters. Using a computer program written for this purpose, and a version of the MINDO[6b] method with parameter functions similar to those in the earlier PNDO[6a] treatment, we were able to find a set of parameters that enable the heats of formation and geometries of hydrocarbons to be estimated simultaneously, with reasonable accuracy. Here we report extensions of this procedure, termed MINDO/2, to compounds containing oxygen and/or nitrogen.

Theoretical Procedure

The MINDO method[6b] is essentially the EMZDO method of Dixon,[7] or the INDO method of Pople, *et al.*,[8] parametrized to give good predictions of ground state properties rather than to mimic the results of *ab initio* SCF MO calculations. In its original form,[6b] no attempt was made to calculate molecular geometries; the core repulsion (CR_{mn}) between atoms m and n was therefore set equal to the corresponding repulsion between the valence electrons (ER_m^n) for a situation where the valence shell AO's are occupied in a manner corresponding to the valence states of neutral atoms m and n. This approximation had already been used successfully in our SCF π MO treatment;[5] there, of course, no difficulties arise over the geometry since this is determined by a rigid skeleton of localized σ bonds. The electron core attractions, V_{in}, were likewise set equal to *minus* the repulsion between an electron in the AO i and the valence electrons of atom n in its appropriate neutral valence state. The one-electron integrals W_i, (ii,ii), and (ij,ij) (i and j being AO's of the same atom) are found by standard procedures from spectroscopic data for atoms, and the two-center repulsion integrals (ii,kk) (i and k being AO's of two different atoms), from the Ohno–Klopman expression.[6,9] The only "molecular" parameters in the treatment are those in the parametric expression for β_{ij}^c, the one-electron core resonance integral between AO's i and j.

In the MINDO/2 method,[1] the same expressions are used for everything except the core repulsion and the core resonance integrals β_{ij}^c. The expression for CR_{mn} is that used in the PNDO treatment,[6a] *i.e.*

$$CR_{mn} = ER_{mn} + (Z_mZ_ne^2/r_{mn} - ER_{mn})e^{-\alpha r_{mn}} \quad (1)$$

where Z_me and Z_ne are the core charges on atoms m and n, respectively, r_{mn} is the corresponding internuclear distance, and α is a parameter characteristic of the pair of atoms. The expression for β_{ij}^c is essentially the Mulliken approximation

$$\beta_{ij}^c = BS_{ij}(I_i + I_j) \quad (2)$$

where I_i and I_j are the valence state ionization potentials of the AO's i and j, S_{ij} is the corresponding overlap integral (calculated using Slater–Zener AO's), and B is a parameter characteristic of the two atoms involved (but independent of the particular AO's). There are

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[1] Part IX: M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

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[3] Robert A. Welch Postdoctoral Fellow.

[4] On leave of absence from The Chemical-Pharmaceutical Research Institute, Cluj, Romania.

[5] A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965); M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685 (1965); M. J. S. Dewar and C. de Llano, *ibid.*, **91**, 789 (1969); M. J. S. Dewar and T. Morita, *ibid.*, **91**, 796 (1969), and papers cited in the last two references.

[6] (a) M. J. S. Dewar and G. Klopman, *ibid.*, **89**, 3089 (1967); (b) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); (c) N. C. Baird, M. J. S. Dewar, and R. Sustmann, *ibid.*, **50**, 1275 (1969); (d) M. J. S. Dewar, M. Shanshal, and S. D. Worley, *J. Amer. Chem. Soc.*, **91**, 3590 (1969).

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[8] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

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then two parameters (α and B) for each pair of atoms, or altogether $k(k + 1)$ parameters for a system composed of k different kinds of atoms.

The parametrization program[1] operates by fitting the heats of formation of a set of standard molecules, and the length of one selected bond in each, by a least-squares procedure. Initially the program was limited to 20 molecules; in extending the treatment from C and H (6 parameters) to C, H, and O (12 parameters) we thought it best to use the parameters for C and H established previously[1] in order to keep the number of molecules much greater than the number of parameters to be determined. Later, by using the whole available space in the magnetic core of the CDC 6600 computer of the University of Texas Computation Center, we were able to extend the molecule set to 40. We were then able to determine the 20 parameters for C, H, N, and O simultaneously in a single calculation.

Results and Discussions

Our first approach, with the original parametrization program,[1] involved fitting the heat of formation and the length of the indicated bond for each of the 19 molecules listed in Table I. Note that in several cases a given molecule appears more than once, different bonds being used in the parametrization. As in part IX,[1] problems arose in the case of bonds involving hydrogen, the calculated bond lengths being systematically too large for any choice of parameters that gave good energies. In the earlier work,[1] we were consequently forced to fit our calculations to models in which the lengths of all the CH bonds were greater than the experimental values by 0.1 Å; here we were forced to adopt a similar and slightly larger offset (0.15 Å) in the lengths of OH bonds. Fortunately, as pointed out previously,[1] these systematic errors in the lengths of CH and OH bonds are not serious from a chemical standpoint because they do not alter the overall geometry, hydrogen being univalent.

Table I compares calculated and observed heats of formation for the 19 systems indicated, and calculated and observed lengths of the indicated bonds. In the case of OH, the calculated bond lengths have been corrected for the 0.15-Å offset. Note that in cases where a given molecule is included more than once, the calculated heats of formation differ. This is because the calculated value corresponds to a geometry in which all bonds other than the one indicated in the first column of Table I have their assumed lengths (*i.e.*, experimental values for CC, CO, and OO, experiment + 0.1 Å for CH, and experiment + 0.15 Å for OH), but in which the length of the remaining bond is chosen to minimize the calculated energy. Unless these "calculated" lengths agree with the values assumed, the calculated energies then refer to different geometries. The parameters derived from the parametrization program, and used to calculate the values listed in Table I, are shown in Table II.

The agreement between the calculated and observed heats of formation (average error, 3.2 kcal/mol) and calculated and observed bond lengths (average error, 0.020 Å, allowing for the 0.15-Å offset for OH bonds) is satisfactory, being comparable with that previously attained[1] for hydrocarbons. As a further check, we carried out more extensive calculations for the molecules and ions listed in Table III, minimizing the energy with respect to simultaneous variation in the lengths of all the bonds, but assuming experimental bond angles. The agreement between the calculated and observed heats of formation, and bond lengths, is quite reasonable.

Table I. Heats of Formation and Bond Lengths

Compound (bond)	Heats of formation, kcal/mol at 25° Obsd	Calcd	Bond length, Å Obsd[a]	Calcd[b]
H_2O (OH)	−57.80[c]	−54.13	0.957	0.967
H_2O_2 (OH)	−32.53[c]	−32.74	0.970	0.983
CH_3OH (CO)	−48.08[c]	−49.82	1.428	1.395
CH_3OH (OH)	−48.08[d]	−49.38	0.960	0.974
CH_3CH_2OH (OH)	−56.24[d]	−60.70	0.960	0.974
HCOOH (C—O)	−90.49[d]	−90.44	1.312	1.348
HCOOH (C=O)	−90.49[d]	−89.28	1.245	1.247
HCOOH (OH)	−90.49[d]	−90.14	0.950	0.984
CH_3COOH (C=O)	−103.80[d]	−104.22	1.245	1.255
CH_2COOH (C—O)	−103.80[d]	−104.11	1.312	1.336
CH_2CO (CO)	−14.60[e]	−20.33	1.161	1.190
CH_2O (CO)	−27.70[d]	−19.66	1.210	1.226
CH_3CHO (CO)	−39.67[d]	−44.39	1.216	1.228
CH_3OCH_3 (CO)	−44.30[d]	−37.33	1.416	1.404
CH_3COCH_3 (CO)	−51.72[d]	−56.31	1.215	1.232
CH_3OOCH (C—O)	−81.00[d]	−82.82	1.334	1.347
CH_3OOCH (CH_3—O)	−81.00[d]	−83.02	1.437	1.412
CH_3OOCH (C=O)	−94.04[c]	−84.48	1.200	1.235
CO_2 (CO)	−94.04[c]	−91.44	1.162	1.189

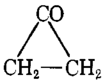
[a] L. E. Sutton, Ed., "Table of Interatomic Distances and Configurations in Molecules and Ions," Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965. [b] Values listed for OH bonds are 0.15 Å less than calculated. [c] "JANAF Thermochemical Tables," D. R. Stull, Ed., The Dow Chemical Co., Midland, Mich., 1965. [d] L. H. S. Green, *Quart. Rev.* (London), **15**, 125 (1961). [e] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

Table II. Parameters for C, H, and O

Elements	CC	CH	HH	CO	OO	OH
B	0.36862	0.34104	0.48328	0.45310	0.66852	0.53378
α, Å^{-1}	1.6343	1.1843	0.6653	1.7557	1.5073	0.9262

The procedure used here[1] also gives estimates of force constants. While the values found in this way for bonds involving oxygen were in less good agreement with experiment than in the case of hydrocarbons,[1] being systematically too large by 30–40%, the agreement was still much closer than that given by other methods. Thus the values for CO stretching in formaldehyde, in mdyn/Å, are MINDO/2, 17.9; CNDO/2,[10] 34.1; obsd,[11] 12.1. Other typical examples are OH in H_2O, calcd, 9.9, obsd,[11] 7.76; CO in CO_2, calcd, 24.3, obsd,[11] 16.8; CO in ethers and alcohols, calcd, 7.1–8.4, obsd,[11] 5.0–5.8; C=O in addehydes and ketones, calcd, 15.2–17.2, obsd,[11] 11.8–13.4.

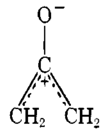
Detailed calculations were next carried out for two compounds of current interest, cyclopropanone (I) and carbon suboxide (II).



I

$O=C=C=C=O$

II



III

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[11] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

Table III. MINDO/2 Calculations for Oxygen Compounds

Compound	Heats of formation, kcal/mol at 25° Calcd	Obsd	Bond lengths, Å, calcd (obsd^a)
$CH_2{=}C{=}O$	−20.37	-14.60^b	CH 1.091 (1.083), CC 1.308 (1.304), CO 1.189 (1.161)
HCOOH	−91.10	-90.69^c	C=O 1.241 (1.245), CO 1.345 (1.312), OH 0.981 (0.960)
CH_3OH	−50.03	-48.08^c	CO 1.400 (1.428), OH 0.974 (0.960)
CH_2O	−19.62	-27.70^c	CO 1.224 (1.210), CH 1.125 (1.120)
$O{=}C{=}C{=}O$	−20.23		CC 1.291 (n.a.), CO 1.198 (n.a.)
$O{=}C{=}C{=}C{=}O$	−41.89	-23.38^d -47.4^e	CC 1.278 (1.294 ± 0.015),^{f} CO 1.187 (1.168 ± 0.009^f), CCO 2.465 (2.462^f)
$CH_3OH_2^+$	130.61	$136,^g$ 127.2^h	CO 1.455 (n.a.), OH 0.994 (n.a.)
$H_2C{=}OH^+$	158.45	$175,^i$ $176,^j$ 174.25^h	CH 1.115 (n.a.), CO 1.274 (n.a.), OH 0.983 (n.a.)
HCO^+	202.42	207^k	CH 1.085 (n.a.), CO 1.139 (n.a.)

[a] See ref *a* of Table I. [b] See ref *c* of Table I. [c] See ref *d* of Table I. [d] B. D. Kybett, G. K. Johnson, C. K. Barker, and J. L. Margrave, *J. Phys. Chem.*, **69**, 3603 (1965). [e] O. Glemser, "Handbook of Preparative Inorganic Chemistry," Vol. I, G. Brauer, Ed., Academic Press, New York, N. Y., 1963. [f] A. Almenningen, S. P. Arnesen, O. Bastiansen, H. M. Seip, and R. Seip, *Chem. Phys. Lett.*, **1**, 569 (1968). [g] V. L. Tal'roze, *Pure Appl. Chem.*, **5**, 455 (1962). [h] Calculated by MINDO/1, see N. Bodor and M. J. S. Dewar, *Tetrahedron*, in press. [i] M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.*, **68**, 3191 (1964). [j] A. G. Harrison, A. Tvko, and D. van Raalte, *Can. J. Chem.*, **44**, 1625 (1966). [k] H. Pritchard and A. G. Harrison, *J. Chem. Phys.*, **48**, 2827 (1968).

Some years ago Burr and Dewar[12] postulated the occurrence of a nonclassical mesoionic intermediate (III) in the Favorskii rearrangement, III subsequently cyclizing to the isomeric cyclopropanone I. This mechanism, based on simple HMO calculations, seems to have been confirmed experimentally.[13] Recently, however, Hoffmann[14] has concluded on the basis of extended Hückel calculations that III should be more stable than I. While the subsequent demonstration[15] that I can exist as a stable species in the gas phase seems to invalidate Hoffmann's suggestion, we thought it of interest to calculate the properties of I and III by the method indicated above. As expected, this predicts I to be very much more stable than III (heats of formation, −34.1 and +44.1 kcal/mol, respectively). While the MINDO/2 method seems to underestimate strain energies in cyclopropane derivatives, giving heats of formation that are too negative by 8–10 kcal/mol, the calculated difference in heat of formation between I and III is a whole order of magnitude greater than this. Moreover, the geometry calculated for I agrees closely with that given by a recent electron diffraction study[15] (bond lengths (Å), calcd (obsd): $OC{-}CH_2$, 1.471 (1.475 ± 0.017); $H_2C{-}CH_2$, 1.555 (1.575 ± 0.012); C=O, 1.211 (1.191 ± 0.020); CH, 1.104 (1.086 ± 0.025)). Thus there seems no doubt that I must be more stable than III and that Hoffmann's prediction[14] serves as yet another indication of the unreliability of the extended Hückel method.

A second interesting problem is presented by a recent electron diffraction study of II by Bastiansen, *et al.*,[16] the results of which are incompatible with a simple linear geometry. The OO distance and the longer CO distances were less than those predicted for a linear molecule with the observed CC and CO bond lengths and were also temperature dependent. The results could be explained in terms of facile bending vibrations of an inherently linear molecule. The intermediate CO distances (*i.e.*, CCO) were moreover normal and independent of temperature, implying that bending takes place about the central carbon atom.

As indicated in Table III, the bond lengths and intermediate CO distances predicted for II are in good agreement with experiment, the calculations being for the predicted linear equilibrium configuration. We also calculated the energy of II for various bent configurations; the variations in energy with bond angle lead to the following values for the bending force constants (mdyn/Å): $f(\text{CCO}) = 1.70$, $f(\text{CCC}) = 0.77$. It will be seen that the force constant for bending about the central carbon is indeed much the lower, and also that its value is near the lower limit of the usual range (0.5–2 mdyn/Å) for bending force constants.

One flaw in this approach, which was pointed out in the preceding paper,[1] is the fact that there were several different sets of parameters for hydrocarbons which gave comparable results. There is no guarantee that this degeneracy of solutions will hold for other compounds; indeed, attempts to extend the present treatment to nitrogen proved unsatisfactory. Since in the meantime we had succeeded in extending the parametrization program to include 40 molecules, we decided to try parametrizing C, H, O, and N simultaneously, without making any prior assumption. Here 20 parameters in all are involved; these should be sufficiently overdetermined by use of a set of 40 dissimilar molecules (*i.e.*, 80 pieces of information to determine 20 parameters).

Table IV shows the 40 standard molecules used in this investigation, together with the calculated and observed heats of formation and bond lengths. As before, the calculations were fitted to models in which bond lengths not involving hydrogen were experimental values, whereas bonds involving hydrogen were taken to be longer. The offset for NH bonds was taken to be the same as for CH, *i.e.*, 0.1 Å (*cf.* Table II), while the offset for OH bonds was as before (Table II), *i.e.*, 0.15 Å. The "calculated" bond lengths in Table IV are corrected for these offsets.

Comparison with part IX[1] and Table I shows that the agreement with experiment is at least as good as before for hydrocarbons and for compounds containing carbon,

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(12) J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).

(13) A. W. Fort, *J. Amer. Chem. Soc.*, **84**, 4979 (1962).

(14) R. Hoffmann, *ibid.*, **90**, 1475 (1968).

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(16) A. Almenningen, S. P. Arnesen, O. Bastiansen, H. M. Seip, and R. Seip, *Chem. Phys. Lett.*, **1**, 569 (1968), and personal communication from Professor O. Bastiansen, to whom we are grateful for drawing our attention to this problem.

Table IV. Heats of Formation, Bond Lengths, Force Constants, and Ionization

	Potentials of compounds containing C, H, O, and N								
	Heat of formation, kcal/mol at 25°		Bond length, Å		Force constant, mdyn/Å		Ionization potential		
Compound (bond)	Obsd	Calcd	Obsd[a]	Calcd[b]	Obsd	Calcd	Obsd	Calcd (a)[c]	Calcd (b)[d]
Methane (CH)	−17.9[e]	−16.2	1.093	1.100	5.0[f]	5.8	12.70[g]	12.83	13.16
Ethane (CC)	−20.2[e]	−21.7	1.543	1.512	4.5[f]	4.9	11.56[g]	11.17	11.46
Ethane (CH)	−20.2[e]	−22.2	1.093	1.109	4.8[f]	5.7	11.56[g]	11.17	11.46
Ethylene (CC)	12.5[e]	14.4	1.337	1.317	9.6[f]	9.3	10.51[g]	11.08	10.58
Ethylene (CH)	12.5[e]	14.6	1.086	1.094	5.1[f]	5.7	10.51[g]	11.08	10.58
Acetylene (CC)	54.3[e]	57.7	1.204	1.186	15.8[f]	15.1	11.40[h]	10.64	10.90
Acetylene (CH)	54.3	58.0	1.058	1.061	5.9	6.1	11.40[h]	10.64	10.90
Benzene (CH)	19.8[e]	19.8	1.084	1.102		5.6	9.25[i]	9.78	9.57
Toluene (CMe)	11.9[e]	11.7	1.510	1.497		5.1	8.82[j]	8.71	9.23
Cyclopentane (CC)	−18.5[e]	−26.5	1.534	1.530		5.5	10.49[j]	10.04	10.42
Cyclohexane (CC)	−29.4[e]	−28.2	1.540	1.537		5.7	9.81[j]	9.49	9.85
Isobutane (CC)	−32.2[e]	−25.0	1.534	1.534		5.6	10.40[j]	10.25	10.71
Water (OH)	−57.8[k]	−58.9	0.957	0.972	7.8[l]	10.1	12.62[j]	11.77	12.20
H_2O_2 (OH)	−32.5[m]	−32.9	0.970	0.984		9.0		11.29	11.43
CH_3OH (OH)	−48[n]	−51.8	0.960	0.973	7.6[l]	9.5	10.83[j]	10.61	10.96
CH_2O (C=O)	−27.7[k,n]	−22.4	1.210	1.211	12.3[l]	16.5	10.80[o]	10.47	10.80
CH_3CHO (C=O)	−39.7[k,n]	−42.8	1.216	1.216		15.9	10.20[j]	10.00	10.43
CH_3COCH_3 (C=O)	−51.7[n]	−56.6	1.215	1.216		15.8	9.68[j]	9.51	9.96
HCOOH (C—O)	−90.5[n]	−89.9	1.312	1.338		11.3		10.68	11.21
HCOOH (C=O)	−90.5[n]	−89.4	1.245	1.235		14.0		10.68	11.21
CH_3OOCH (Me—O)	−81.0[n]	−82.7	1.334	1.337		9.6		10.41	10.91
CH_3OCH_3 (CO)	−44.3	−40.3	1.416	1.390		7.9	9.94[j]	9.72	10.39
CO_2 (CO)	−94.0[k]	−92.9	1.162	1.179	16.8[f]	22.7	13.68[p]	12.91	12.92
CH_2CO (CO)	−14.6[q]	−22.1	1.161	1.176		20.2		9.44	9.71
CH_3NH_2 (CN)	−6.7[k]	−9.0	1.474	1.435		5.7	9.18[p]	9.47	9.86
$CH_3CH_2NH_2$ (CN)	−11.6[k]	−14.0	1.472	1.444		5.7	9.19[p]	9.31	9.74
$CH_3CH_2NH_2$ (NH)	−11.6[k]	−13.9	1.012	1.025		7.5	9.19[p]	9.31	9.74
H_2NNH_2 (NH)	22.7[k]	17.0	1.022	1.021		7.06		9.48	9.72
NH_3 (NH_3)	−11.0[k]	−11.2	0.912	0.918	6.4[f]	7.7	10.16[p]	10.29	10.48
NH_4^+ (NH)	150.0[q,r]	155.9	1.032	1.036	5.5[f,s]	7.5			
CH_3NHNH_2 (NH)	23.3[t]	21.2	1.022	1.024		7.0		9.01	9.49
$CH_3NHNHCH_3$ (CN)	22.8[u]	24.7	1.472	1.438		5.6		8.79	9.36
$CH_3NHNHCH_3$ (NH)	22.8[u]	25.6	1.022	1.030		6.8		8.79	9.36
Aniline (CN)	20.8[v]	23.8	1.430	1.420		6.4	7.71[w]	8.37	8.79
HNO_3 (HOON—O)	−32.1[q]	−36.4	1.22	1.208		15.8		12.51	12.81
HNO_2 (OH)	−18.8[k]	−12.7	0.980	0.969	7.4[x]	8.4		10.99	11.11
N_2O_4 (NO)	2.5[y]	5.0	1.180	1.184		20.1		11.06	11.21
N_2O (NO)	19.5[q]	17.2	1.188	1.138	11.4[z]	14.4	12.82[p]	12.07	12.05
CH_3NO_2 (CN)	−12.2[aa]	−14.8	1.47	1.485		6.0	11.23[bb]	11.45	11.59
CH_3NO_2 (NO)	−12.2[aa]	−15.1	1.22	1.205		15.8	11.23[bb]	11.45	11.59

[a] L. E. Sutton, Ed., "Table of Interatomic Distances," Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965.

[b] Calculated values for CH and NH bonds reduced by 0.1 Å, for OH bonds by 0.15 Å.

[c] Calculated by difference from the heats of formation of the molecule and its ion.

[d] From Koopmans' theorem.

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Table V. Parameters for C, H, O, N

Elements	HH	CH	CC	HN	CN	NN	HO	CO	OO	NO
B	0.35869	0.33382	0.35410	0.37556	0.36137	0.29963	0.54268	0.43562	0.68733	0.42679
α, Å^{-1}	0.7535	1.2475	1.7345	1.4204	1.8551	3.1459	0.9073	1.8657	1.4547	2.1550

hydrogen, and oxygen, and also that the results for compounds containing nitrogen are of comparable accuracy. The average overall error in heats of formation is 2.8 kcal/mol and in bond length 0.013 Å. The parameters used in these calculations are listed in Table V. Note that the values for C and H are somewhat different from those used previously (part IX[1] and Table II). The present set corresponds closely to one of the possible alternatives originally considered.[1]

The last five columns of Table IV compare observed

Table VI. Heats of Formation and Molecular Geometries

	Heat of formation, kcal/mol Obsd[a]	Calcd	Bond lengths, Å, calcd (obsd)	Ref
Ethane	−20.2	−22.8	C—C 1.506 (1.534), C—H 1.116 (1.093)	*n*
Ethane (eclipsed)	−17.3[b]	−20.4	C—C 1.517 (n.a.), C—H 1.114 (n.a.)	
trans-Butadiene	26.3[c]	30.9	C═C 1.329 (1.343), C—C 1.455 (1.467)	*o*
cis-Butadiene	28.6[d]	34.0	C═C 1.331 (n.a.), C—C 1.469 (n.a.)	
Cyclohexane (chair)	−29.4[c]	−31.3	C—C 1.524 (1.534), C—H 1.119 (n.a.)	*p*
Cyclohexane (boat)	−24.1[e]	−25.4	C—C 1.529 (n.a.), C—H 1.126 (n.a.)	
Cyclopropane	+12.7[f]	−1.1	C—C 1.496 (1.51), C—H 1.113 (1.089)	*q*
Cyclobutane	6.4[f]	+18.7	C—C 1.531 (1.548), C—H 1.141 (1.092)	*r*
Amidogen	40.3[g]	33.2	N—H 1.006 (1.024), ∠HNH 131.2° (103.3°)	*n*
Methylamine	−6.7[c]	−9.6	C—H 1.109 (1.093), C—N 1.432 (1.474), N—H 1.022 (1.014)	*n*
Ethylenimine	30.1[h]	27.7	N—H 1.03 (1.0 assigned), C—N 1.455 (1.488), C—C 1.542 (1.480)	*n*
Trimethylamine	−5.2[i]	3.3	C—N 1.453 (1.472), C—H 1.117 (1.09 assigned)	*n*
Formic acid	−90.5[a]	−90.6	C═O 1.230 (1.245), C—O 1.338 (1.312), O—H 0.979 (0.950)	*n*
Methyl formate	−81.0[a]	−84.5	C═O 1.224 (1.200), C—O 1.334 (1.334), C—O_{CH_3} 1.392 (1.437)	*n*
Formaldehyde	−27.7[a]	−22.5	C—H 1.120 (1.121), C═O 1.209 (1.210)	*n*
Methanol	−48.1[a]	−53.3	C—O 1.374 (1.428), O—H 0.974 (0.960), dihedral angle of H—C_{CH_3} with OH 60° (60°)	*n*
Methanol (protonated)	136[j]	127.9	C—O 1.448 (1.428), O—H 0.995 (0.970)	*s*
Formaldehyde (protonated)	175[k] 176 ± 3[l]	155.5	C—H 1.111 (1.120), C═O 1.259 (n.a.), O—H 0.982 (0.970)	*s*
Nitrate ion (NO_3^-)	−89 ± 5[m]	−95.8	N—O 1.239 (1.241) (found to be planar in agreement with experiment)	*t*
Nitrite ion (NO_2^-)		−48.2	N—O 1.215 (1.240), ∠ONO 115° (111.4°)	*u*
Nitrogen dioxide	−8.1[c]	−10.9	N—O 1.173 (1.189)	*v*
Hydrogen isocyanate		−13.9	N—H 1.000 (0.987 ± 0.01), N—C 1.230 (1.207 ± 0.01), C—O 1.170 (1.171 ± 0.01)	*n*
Formaldoxime		3.4	C—N 1.286 (1.27, 1.29), N—O 1.350 (1.36)	*w*
Nitramide		−29.2	N—H 1.016 (1.020), N—O 1.192 (1.180)	*n*
Nitrogen tetroxide	2.5[a]	−0.02	N—O 1.184 (1.180), ∠ONO 134.6° (133.7°)	*x*
	−76.3[c]	−78.4	C═O 1.21 (n.a.), N—H 1.020 (1.036)	*n*
Nitric acid	−32.2[a]	−36.4	N···O 1.206 (1.22 ± 0.02), O—H 0.979 (0.980), ∠ONO 130° (130 ± 5°)	*n*
Formamide		−50.7	N—H 1.020 (0.995 ± 0.007), C—N 1.380 (1.343 ± 0.007), C═O 1.220 (1.243 ± 0.007)	*n*

[a] See references given in Table IV. [b] Calculated from the value for staggered ethane using the experimentally determined height (2.9 kcal/mol) of the rotational barrier; see D. R. Lide, *J. Chem. Phys.*, **29**, 1426 (1958). [c] "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, The Carnegie Press, Pittsburgh, Pa., 1953. [d] See text below and ref 19. [e] Calculated from the value for the chair conformation using the experimental value (5.2 kcal/mol) for the heat of conversion to the boat conformation; see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962. [f] H. A. Skinner and G. Pilcher, *Quart. Rev.* (London), **17**, 264 (1963). [g] "JANAF Thermochemical Tables," D. R. Stull, Ed., The Dow Chemical Co., Midland, Mich., 1965. [h] A. A. Vredenskii, T. N. Masalitinova, and Yu. A. Katin, *Russ. J. Phys. Chem.*, **40**, 1050 (1966). [i] C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962. [j] V. Tal'roze, *Pure Appl. Chem.*, **5**, 455 (1962). [k] M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.*, **68**, 3191 (1964). [l] A. G. Harrison, A. Ivko, and D. Van Raalte, *Can. J. Chem.*, **44**, 1625 (1966). [m] H. F. Cordes and W. R. Fetter, *J. Phys. Chem.*, **62**, 1340 (1958). [n] L. E. Sutton, Ed., "Table of Interatomic Distances," Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965. [o] W. Hangen and L. M. Traetteberg, *Acta Chem. Scand.*, **20**, 1726 (1966). [p] M. I. Davis and O. Hassel, *ibid.*, **18**, 813 (1964). [q] O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964). [r] A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961). [s] Standard bond lengths. [t] N. B. H. Jonathan, *J. Mol. Spectrosc.*, **4**, 75 (1960). [u] G. Carpenter, *Acta Crystallogr.*, **5**, 132 (1952); M. Truter, *ibid.*, **7**, 73 (1954). [v] G. Moore, *J. Opt. Soc. Amer.*, **43**, 1045 (1953). [w] I. N. Levine, *J. Mol. Spectrosc.*, **8**, 276 (1962); W. C. Hamilton, *Acta Crystallogr.*, **14**, 95 (1961). [x] D. W. Smith and K. Hedberg, *J. Chem. Phys.*, **25**, 1282 (1956).

force constants with those calculated for the relevant bonds, and observed ionization potentials with values calculated directly by difference in heat of formation between the molecule and its derived ion and values estimated from orbital energies using Koopmans' theorem. The values for ion radicals were calculated by the "half-electron" method,[17] which was shown previously[1] to give good values for the heats of formation of radicals and ion radicals in the MINDO/2 method.

It will be seen that the agreement between the calculated and observed force constants for hydrocarbons is excellent, even better than before. In the case of compounds containing oxygen, the calculated values are again systematically too high but this time by a smaller margin. The calculated force constants for bonds involving nitrogen are about as good as those for oxygen. As we pointed out in part IX,[1] other procedures have given very poor predictions of force constants.

The agreement between the calculated and observed ionization potentials is also very satisfactory, particularly for the values estimated by difference between the molecule and its ion. As was pointed out in part IX,[1] other methods have usually given very poor estimates of ionization potentials for polyatomic organic molecules. The experimental values listed in Table IV were determined by photoelectron spectroscopy and should be reliable at least to ±0.1 eV. Most of the earlier values in the literature were determined by electron impact methods and are subject to relatively large and uncertain errors.

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[17] M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, **90**, 1959 (1968).

More detailed calculations were carried out for the 28 molecules listed in Table VI, the geometries being minimized for simultaneous variation of the lengths of all the bonds. The calculated lengths of bonds involving hydrogen have again been corrected for the offsets indicated above.

The agreement between the calculated and observed heats of formation and bond lengths is again very satisfactory, the errors in the former being usually less than 5 kcal/mol and in the latter rarely greater than 0.02 Å. The values for hydrocarbons are particularly interesting in that the present set of parameters seems to give a better account of conformational effects than those in the previous paper.[1] Thus the predicted barrier to rotation in ethane (2.4 kcal/mol) and the difference in energy between the chair and boat forms of cyclohexane 5.9 kcal/mol) are in good agreement with experiment (2.9 and 5.3 kcal/mol, respectively), whereas the earlier[1] treatment gave estimates that were too low. The predicted difference in energy between the *cis* and *trans* forms of 1,3-butadiene (3.1 kcal/mol) is also close to that estimated by Aston[18] for the difference in energy between the stable *trans* form and the unstable rotamer (2.3 kcal/mol). Aston assumed the latter to be the *cis*-planar isomer, although this has not been established. Note also that the proton affinities of several oxygen compounds are well predicted. The only serious errors occur in the case of cyclopropane and cyclobutane, where the strain energy is again[1] underestimated by 12–13 kcal/mol, and in nitrogen dioxide, a rather unusual radical.

The fact that the present procedure seems to account better for nonbonded interactions is also reflected in the better values it gives for HCH bond angles. The values are still too small but are closer to experiment than the values given by the previous[1] treatment (Table VII).

Table VII. Calculated and Observed HCH Bond Angles

Compound	HCH bond angle Part IX[1]	This paper	Obsd[a]
Ethane	101	106.8	109.5
Ethylene	106	111.6	115.6

[a] See ref *a* of Table I.

The second set of parameters thus seems to be somewhat superior to the first, particularly in view of the inclusion of nitrogen. It did not, however, seem worthwhile to repeat the calculations for cyclopropanone and carbon suboxide since the results given by the two procedures are so similar in cases where they overlap.

Summary and Conclusions

The present procedure thus not only extends MINDO/2 to compounds containing nitrogen and/or oxygen, but it also seems to give a somewhat better description of hydrocarbons than did the previous version.[1] In view of the apparent success of the latter in predicting potential surfaces for some simple reactions of hydrocarbons, there seems to be good reason to hope that the present treatment may prove useful in the study of reaction mechanisms and chemical reactivity for a very wide range of organic molecules. It also seems likely that the treatment should apply equally well to compounds containing other elements and studies to this effect are in progress.

The present treatment does, however, suffer from several obvious deficiencies. Thus the errors in the heats of formation, while smaller by orders of magnitude than those given by other procedures, are still too large. In particular, the results for cyclopropane and cyclobutane suggest that strain energies are underestimated, as in the earlier version[1] and in contrast with PNDO[6a] or MINDO/1.[6b] Curiously enough the heat of formation of ethylenimine was correctly predicted. Problems also arise in the case of bonds involving hydrogen, where the lengths are systematically overestimated. And finally, the method fails to give a good account of compounds such as H_2O_2, NH_2OH, or N_2H_4, in which two second-row atoms carrying lone pairs are directly linked. The heats of formation of such compounds are correctly predicted if the lengths of the OO, NO, or NN bonds are assumed, but the calculated bond lengths are too short and the heats of formation calculated for these lengths are too negative.

The last failing is probably inherent in the MINDO treatment, owing to its neglect of two-center integrals involving one-center overlap. In the conventional picture, the lone pair electrons in nitrogen and oxygen are supposed to occupy hybrid AO's and so to give rise to relatively large dipole moments. The bonds between pairs of such atoms are lengthened and weakened by the resulting dipole–dipole repulsions. In the expression for the total energy in the full Roothaan SCF LACO MO treatment, such dipole–dipole repulsions correspond to terms involving integrals of the type (sp, s′p′) where s and p are 2s and 2p AO's of one atom, and s′ and p′ AO's of the other. These integrals are neglected in the MINDO treatment.[19]

While this last difficulty could be avoided by adopting a procedure (*e.g.*, NDDO) in which such integrals are included, the penalty would be a great increase in complexity and computing time. For the present it seems better to accept the limitation in order that calculations may be carried out without unreasonable expense for systems large enough to be of real chemical interest. The other weaknesses of MINDO/2 are probably not inherent and may well be remedied by a better parametrization. However, even in the present form, the method should have wide applications.

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(18) J. G. Aston, *Discuss. Faraday Soc.*, 10, 73 (1951).

(19) For a detailed discussion see M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969.