Ground States of Molecules. XXVII. MINDO/3 Calculations for CHON Species[1,2]

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Abstract: The MINDO/3 method has been tested by calculations for a wide range of compounds derived from C, H, O, and N. The calculated heats of formation, molecular geometries, and dipole moments agree quite well with experiment; errors occur in compounds where hydrogen atoms are crowded together, where triple bonds are present, or where adjacent pairs of atoms have unshared pairs of electrons. The worst errors of MINDO/2 and MINDO/2' are, however, avoided; thus good results are obtained for diatomic molecules and heteroaromatic compounds.

The two preceding papers[1,3] of this series have described the development of an improved version (MINDO/3) of the MINDO semiempirical SCF-MO treatment[4,5] and extensive calculations for hydrocarbons using it. Here we report similar calculations for compounds containing nitrogen and oxygen. The calculations were carried out as before,[1] using the parameters previously reported,[3] on the CDC 6400/6600 computer at The University of Texas computation center. All geometries were calculated by complete minimization of the energy with respect to all geometrical variables, no assumptions of any kind being made.

The calculated heats of atomization were as usual[1,4] converted to heats of formation, using the following experimental values for the heats of formation of gaseous atoms: C, 170.89; H, 52.102; N, 113.0; O, 59.559 kcal/mol. The heats of formation calculated in this way are compared with experiment in Table I while Table II shows a similar comparison of calculated with observed geometries.

The agreement between the calculated and observed heats of formation is much the same as it was for hydrocarbons, *i.e.,* generally satisfactory but with similar specific exceptions. Thus the heat of formation calculated for trimethylamine is much too positive; this is presumably due to the tendency (noted previously[1]) of MINDO/3 to overestimate nonbonded hydrogen–hydrogen repulsions. This would also account for the incorrect prediction (Table II) that the molecule is planar instead of pyramidal. Likewise cyanoacetylene exhibits in a massive way the apparent tendency[1] of MINDO/3 to overestimate the strengths of triple bonds. These effects were also seen in hydrocarbons; a third, specific to compounds with adjacent atoms carrying lone pairs of electrons, appears in compounds such as hydrazine or hydrogen peroxide. In the INDO approximation, on which MINDO is based, the integrals describing the dipole fields, due to lone pair electrons in hybrid AOs, are neglected. As a result the dipole–dipole repulsions in compounds such as hydrazine are neglected and their calculated heats of formation are consequently too negative. As one would also expect on this basis, the corresponding bond lengths are underestimated, *e.g..* by 0.14 Å in the case of the NN bond in hydrazine and by 0.12 Å in the case of the OO bond in hydrogen peroxide.

Otherwise, however, the agreement between the calculated and observed heats of formation is quite reasonable and several serious deficiencies of MINDO/2[5] seem to have been overcome. Thus the values for diatomic molecules (N_2, O_2, CO) are now quite well reproduced whereas the MINDO/2 ones were seriously in error and the same is true of a number of heteroaromatic compounds.[6] The value for

O_2 in Table I refers to the $^1\Delta$ state which corresponds best to the single closed shell configuration calculated here. A detailed MINDO/3 study of the various states of O_2 will be found elsewhere.[7] It has been shown that MINDO/3 also gives a good estimate of the energy of the triplet ($^3\Sigma$) ground state.
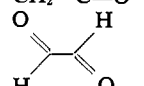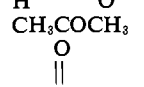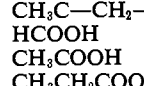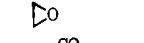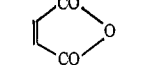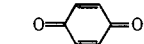
The calculated geometries are also in reasonable agreement with experiment, apart from the case noted above of bonds between atoms with lone pairs of electrons where the calculated values are much too small. Here again the results are much better than those given by MINDO/2[5a] or MINDO/2';[5b] in particular ammonia is now predicted to be pyramidal instead of planar and water bent instead of linear and the MINDO/3 bond angles in both cases agree well with experiment. The same is true of the calculated barrier to inversion in ammonia, the MINDO/3 value (6.0 kcal/mol) being very close to that observed (5.9 kcal/mol[8]). The only semiempirical treatment that had previously given good estimates of such barriers was MINDO/1,[4] in which bond lengths were assumed, not calculated. Nitriles, on the other hand, have been a casualty of the reparametrization, the results for them from MINDO/3 being inferior to those from MINDO/2.

The results for pyrrole and furan are interesting. Not only does MINDO/3 give good estimates of their heats of formation but it also correctly reproduces the difference in geometry between them. Thus the CC bond lengths in furan are correctly predicted to alternate strongly, the structure corresponding closely to that expected for a "localized" butadiene 1,4-oxide, whereas the CC bond lengths in pyrrole are predicted, again correctly, to be more nearly "aromatic."

Several other successes may be noted. Thus the CC bond in oxalic acid, although of sp^2:sp^2 type, is correctly predicted to be of "paraffinic" length. The relative lengths of the three different kinds of CO bond in methyl formate are also correctly predicted as are the bond lengths in CO and CO_2. The only large discrepancy, apart from that pointed out earlier, is in the case of the O_3^- radical anion. Here the calculated values seem much more reasonable than the experimental ones, which were admittedly of uncertain accuracy. It is difficult to believe that the OO bonds in O_3 could be longer than those in O_3^-.

On the basis of EH calculations, Hoffmann[9] has predicted that cyclopropanone (**1**) should be less stable by 1 eV (23 kcal/mol) than the zwitterionic isomer **2**. This would be surprising in view of the characterization[10] of **1** as a stable species and also in view of the apparent formation[11] of derivatives of **2** as intermediates in the Favorskii reaction,

Table I. Calculated and Observed Heats of Formation of Organic Compounds Containing Nitrogen and/or Oxygen

Compd	Heat of Formation, kcal/mol (25°)		
	Calcd	Obsd[a]	Error
N_2	5.2	0	5.2
NH_3	−9.4	−10.9	1.5
N_2H_4	2.7	22.8	−20.1
NH_4^+	153.9	150.0	3.9
CH_3NH_2	−4.9	−5.5	0.6
$CH_3CH_2NH_2$	−14.8	−11.3	−3.5
$(CH_3)_2NH$	4.0	1.0	3.0
$(CH_3)_3N$	20.4	−5.7	26.1
CH_3NHNH_2	12.3	22.6	−10.3
△NH	21.9	30.2	−8.3
$CH_3N=NCH_3$ (trans)	26.2	43	−16.8
HCN	34.4	31.2	3.1
CH_3CN	9.5	21.0	−11.5
Pyridine	34.1	34.6	−0.5
Pyrrole	29.5	24.6[b]	4.9
Aniline	17.9	20.7	−2.8
Benzonitrile	48.9	51.4	−2.5
HC≡C—CN	63.8	91.0	−27.2
$O_2(^1\Delta)$	22.8	22.0	0.8
O_3	39.0	34.0	5.0
H_2O	−53.6	−57.8	4.2
H_2O_2	−31.6	−32.5	0.9
CO	−13.5	−26.4	12.9
CO_2	−95.7	−94.0	−1.7
CH_3OH	−50.1	−48.1	−2.0
CH_3CH_2OH	−64.1	−56.2	−7.9
$(CH_3)_2CHOH$	−67.7	−65.1	−2.6
$(CH_3)_3COH$	−64.6	−74.7	10.1
CH_2O	−25.5	−25.9	0.4
CH_3CHO	−43.6	−39.7	−3.9
$CH_2=C=O$	−20.7	−14.2	−6.5
(enol/structure)	−60.7	−50.7	−10.0
CH_3COCH_3	−53.2	−51.9	−1.3
$CH_3C(O)—CH_2—C(O)CH_3$	−91.4	−90.5	−0.9
HCOOH	−88.6	−90.6	2.0
CH_3COOH	−106.9	−103.3	−3.6
CH_3CH_2COOH	−112.4	−108.4	−4.0
HOOCCOOH	−184.4	−175.0	−9.4
CH_3OCH_3	−41.1	−44.0	2.9
$HCOOCH_3$	−80.9	−83.6	2.7
△O	−26.5	−12.6	−13.9
(anhydride)	−112.2	−95.2	−17.0
Furan	−8.0	−8.3	0.3
Phenol	−28.5	−23.0	−5.5
O=⬡=O	−40.8	−34.4	−6.4
HONO	−13.6	−18.8	5.2
$HONO_2$	−29.4	−32.3	2.9
N_2O_4	−4.2	2.5	−6.7
CH_3NO_2	−10.4	−17.9	7.5
H_2NCHO	−52.1	−46	−6

[a] Unless otherwise indicated the observed values are taken from: (i) "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1965; (ii) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, Y. T. Hernon, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 26 (1969); (iii) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, London, 1970. [b] Calculated from the heats of combustion reported by H. Zimmerman and H. Geisenfelder, *Z. Elektrochem.*, **65**, 368 (1961).

these immediately collapsing to more stable isomers derived from **1**. MINDO/2 calculations[5a] had predicted **2** to be much less stable than **1**; the difference (78.2 kcal/mol) was so large that it could not be attributed to the tendency of MINDO/2 to underestimate strain energies in compounds such as **1**. We have now confirmed this result, using MINDO/3; the calculated heats of formation of **1** and **2** are −19.5 and 46.7 kcal/mol, respectively, **2** thus being the less stable by 66.2 kcal/mol. This value is 12 kcal/mol less than the corresponding MINDO/2 value, as would be expected since MINDO/2 underestimates[5a] strain energies in cyclopropane rings by about this amount. It therefore seems certain that **1** is in fact very much more stable than **2**, again emphasizing the unreliability of the EH method even for qualitative estimates of molecular energies.
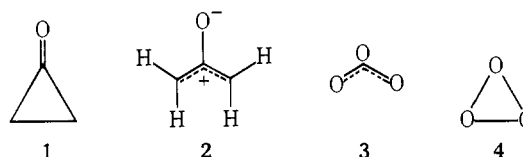
Another interesting comparison is that of ozone (**3**) with the isomeric trioxirane (**4**). We estimate **4** to be less stable than **3** by only 13.1 kcal/mol, implying that **3** may undergo scrambling and other reactions via **4** as an intermediate. Wright[12] has carried out detailed ab initio SCF calculations for O_3, with and without CI. In both cases **4** was predicted to be more stable than **3**. Since ozone has the bent structure **3** and is formed by addition of oxygen atoms to O_2, it seems certain that **3** is more stable than **4**. Here again (cf. ref 1) MINDO/3 appears superior to the ab initio SCF approach for comparing the energies of isomers in which the bonding is different.

Another area where semiempirical methods have proved unsatisfactory is the calculation of dipole moments. Indeed, the values given by ab initio SCF methods are also none too good unless the calculations are carried out using rather large basis sets, and such calculations become prohibitively expensive for any but very small molecules. As Table III shows, the MINDO/3 results are quite reasonably satisfactory in this respect, the agreement with experiment being about as good as for ab initio SCF ones.

The results reported here show that MINDO/3 can be extended to compounds of nitrogen and oxygen with about the same overall accuracy, and with similar provisos, as in the case of hydrocarbons. Earlier semiempirical methods had given such erratic results that they could not be used with any kind of assurance to make quantitative predictions of chemical behavior. While MINDO/2,[5a] and the modified version termed MINDO/2',[5b] were better in this respect, they too broke down in many cases. MINDO/3 seems to be free from most of these deficiences and calculations of reaction paths for a number of reactions involving CHON species have given apparently reasonable results.

Comparisons of MINDO/3 with ab initio SCF methods are difficult because so few calculations have been carried out by the latter with any attempt to calculate molecular geometries.

As we have repeatedly emphasized,[1,4,5,13] calculations of molecular energies without complete optimization of the geometry are quite meaningless in a chemical sense because the use of assumed geometries can lead to errors that are chemically speaking huge. The limited comparisons that are possible (e.g., of **3** with **4**) suggest that MINDO/3 is in fact superior to even rather sophisticated ab initio SCF calculations and of course the computation time required is less by five or six orders of magnitude.

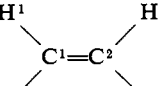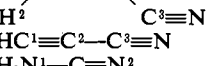**Table II.** Calculated and Observed Molecular Geometries of CHNO Compounds
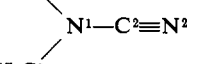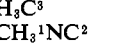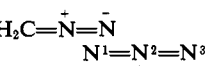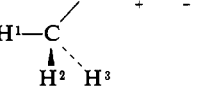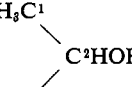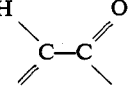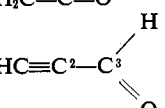
Compd	Ref	Calcd (obsd) molecular geometries[a]
N_2	b	NN, 1.097 (1.098)
NH_3	c	NH, 1.032 (1.012); HNH, 104.6 (106.7)
H_3CNH_2	d	CH, 1.118 (1.093); NH, 1.026 (1.014); CN, 1.404 (1.474); HNC, 112.5 (112.2)
$(H_3C)_2NH$	e,f	CH, 1.122 (1.08); NH, 1.021; CN, 1.393 (1.460), CNC, 129.4 (108, 111)
$(H_3C)_3N$	g	CN, 1.416 (1.472); CH, 1.121 (1.090); CNC, 119.8 (108.7)
$H_3CCH_2NH_2$	f	CN, 1.425 (1.470); CC, 1.507 (1.540); NH, 1.031; C^1H, 1.118; C^2H, 1.110; NCC, 120.5 (110 ± 3)
H_2C $\diagdown$ NH $\diagup$ H_2C	h	CN, 1.457 (1.488); CC, 1.463 (1.480); NH, 1.037 (1.000); CH, 1.112 (1.083); CNH, 116.0 (112); HCC, 153.9 (159.4); HCH, 106.6 (116.6)
H_2NNH_2	i	NN, 1.311 (1.449); NH, 1.055 (1.022); NNH, 115.5 (112.0)
$(CH_3)_2NNH_2$	j	CH, 1.415 (1.470); NN, 1.331 (1.950); NH, 1.052 (1.04 ass.); CH, 1.122 (1.09 ass.); CNN, 118.7 (110 ± 4)
$CH_3NHNHCH_3$	k	CN, 1.426 (1.470); NN, 1.318 (1.450); NH, 1.059 (1.04); CH, 1.121 (1.09 ass.), CNN, 118.9 (110 ± 4); CNNC, 188.6
HCN	l	CN, 1.148 (1.155); CH, 1.096 (1.063)
CH_3CN	l	CN, 1.165 (1.157); CH, 1.118 (1.103); CC, 1.453 (1.458)
H^1 $\diagdown$ $C^1{=}C^2$ $\diagup$ H^2 $\diagdown$ $C^3{\equiv}N$ (with H)	l	C^1C^2, 1.328 (1.340); C^2C^3, 1.441 (1.426); C^3N, 1.161 (1.164); $C^1C^2C^3$, 130.5 (122.6)
$HC^1{\equiv}C^2{-}C^3{\equiv}N$	k	C^1C^2, 1.206 (1.205); C^2C^3, 1.408 (1.378); CN, 1.160 (1.159); CH, 1.072 (1.057)
$H_2N^1{-}C{\equiv}N^2$	m	CN^1; 1.164 (1.178); CN^2, 1.321 (1.328); NH, 1.010 (0.939)
H_3C^1 $\diagdown$ $N^1{-}C^2{\equiv}N^2$ $\diagup$ H_3C^3	n	C^1N^1, 1.422 (1.462); C^2N^1, 1.352 (1.351); C^2N^2, 1.162 (1.160); CH, 1.120 (1.090); C^1NC^3, 118.9 (116.0)
$CH_3{}^1NC^2$	j	C^1N, 1.396 (1.424); C^2N, 1.155 (1.166); HCN, 113.4 (109.1)
$H_2C{=}\overset{+}{N}{=}\overset{-}{N}$	o	CN, 1.274 (1.320); NN, 1.113 (1.120); CH, 1.099 (1.080); HCH, 122.4 (127)
$H^1{-}C$ $N^1{=}\overset{+}{N^2}{=}\overset{-}{N^3}$ H^2 H^3	p	CN, 1.396 (1.470); N^1N^2, 1.184 (1.240); N^2N^3, 1.106 (1.120); CNN, 132.6 (120); H^1CN, 107.4; H^2N, 117.0
$NH_4{}^+$	q	NH, 1.023 (1.032)
Pyridine	r	CN, 1.335 (1.340); C^1C^2, 1.407 (1.395); C^2C^3, 1.406 (1.394); C^1H, 1.114 (1.084); C^2H, 1.105 (1.081); C^3H, 1.107 (1.077)
Pyrazine	s	CN, 1.334 (1.334); CC, 1.406 (1.378); CH, 1.112 (1.05), CCN, 119.6 (122.4); CNC, 120.7 (115.1); CCH, 122.7 (120.3)
Pyrrole	t	CN, 1.368 (1.383); C^1C^2, 1.391 (1.371); C^2C^3, 1.433 (1.429); C^1H, 1.103 (1.075); C^2H, 1.097 (1.075); NH, 1.000 (0.993)
Aniline	u	C^1C^2, 1.426; C^2C^3, 1.398; C^3C^4, 1.402; CC (average), 1.409 (1.392); CN, 1.394 (1.431)
O_2	d	OO, 1.206 (1.207)
O_3	d	OO, 1.253 (1.278); OOO, 126.1 (116.7)
H_2O	v	HO, 0.950 (0.957); HOH, 103.5 (104.5)
H_2O_2	w	OO, 1.381 (1.490); HO, 0.968 (0.970); HOO, 105.5 (100.0)
CH_3OH	x	CO, 1.338 (1.428); OH, 0.950 (0.960); CH, 1.122 (1.095); HOC, 109.0 (109); HCO, 123.4 (111.5)
$H_3C^1H_2C^2OH$	d	C^1C^2, 1.492 (1.54); CO, 1.351 (1.48); C^1H, 1.111 (1.09); C^2H, 1.134 (1.09); OH, 0.951; C^1C^2O, 110.5 (109.5)
H_3C^1 $\diagdown$ C^2HOH $\diagup$ H_3C^3	y	C^1C^2, 1.514 (1.54); CO, 1.369 (1.45); C^1H, 1.112 (1.105); C^2H, 1.139 (1.105); OH, 0.951; $C^1C^2C^3$ 116.3 (112)
$(H_3C)_3COH$	d	CC, 1.535; CO, 1.383; CH, 1.112; OH, 0.951; CCO, 107.6
H_3COCH_3	x	CO, 1.347 (1.416); CH, 1.117 (1.094); COC, 123.4 (111.5)
CH_2O	z	CO, 1.180 (1.210); CH, 1.119 (1.120); HCO, 125.9 (121.0)
$H_3C^1C^2HO$	aa	CC, 1.479 (1.501); CO, 1.193 (1.216); C^1H, 1.111 (1.086); C^2H, 1.140 (1.114); C^1C^2O, 130.1 (123.9); CCH, 120.6 (117.5); HCH, 105.5 (108.3)
H $\diagdown$ O $\diagdown$ $C{-}C$ $\diagup$ $\diagup$ O H	bb	CC, 1.500 (1.47); CO, 1.193 (1.20); CH, 1.132 (1.09); CCO, 124.8 (123 ± 2); HCC, 113.9 (114)
CH_3COCH_3	cc	CC, 1.505 (1.515); CO, 1.208 (1.215); CH, 1.111 (1.086); CCO, 121.3 (121.7); HCC, 112.8 (110.1)
CO	dd	CO, 1.134 (1.128)
CO_2	ee	CO, 1.180 (1.162)
$H_2C{=}C{=}O$	ff	CC, 1.310 (1.314); CO, 1.167 (1.161); CH, 1.086 (1.083); HCH, 122.5 (122.5)
$HC{\equiv}C^2{-}C^3$ $\diagup$ H $\diagdown\diagdown$ O	gg	C^1C^2, 1.207 (1.208); C^2C^3, 1.435 (1.450); C^3O, 1.193 (1.209); C^1H, 1.073 (1.060 ass.); C^3H, 1.134 (1.111 ass.); C^2C^3O, 127.4 (124.3); HC^3O, 122.0 (121.1)

Table II (*Continued*)

Compd	Ref	Calcd (obsd) molecular geometries[a]
(structure: HC with O¹, O²—H)	*d*	CO¹, 1.208 (1.245); CO², 1.322 (1.312); CH, 1.131 (1.085); OH, 0.955 (0.95); HO²C, 114.1 (107.8); HCO¹, 122.8
(structure: H₃C—C with O¹, O²—H)	*hh*	CC, 1.495 (1.497); CO¹, 1.214 (1.245); CO², 1.335 (1.312); O²H, 0.952 (0.95); CH, 1.110 (1.08); CCO¹, 124.4 (119.5); CCO², 106.2; HOC, 108.3 (107.7)
(structure: H—C¹ with O¹, O²—C²H₃)	*ii*	C¹O¹, 1.198 (1.200); C¹O², 1.320 (1.334); C²O², 1.359 (1.437); C¹H, 1.132 (1.101); C²H, 1.119 (1.086); O¹CO², 136.9 (125.8); C¹O²C², 126.8 (114.8)
(structure: H—O¹, C¹—C², ²O, O⁴—H, O³)	*jj*	C¹O¹, 1.330 (1.291); C¹O², 1.212 (1.202); C¹C², 1.551 (1.536); C¹C²O³, 126.4 (121.7); C¹C²O⁴, 105.4 (112.0)
(structure: O¹, C¹—C², H—O², O³, O⁴—H)	*jj*	C¹O¹, 1.213 (1.212); C¹O², 1.330 (1.298); C¹C², 1.548 (1.529); C¹C²O³, 119.8 (119.6); C¹C²O⁴, 112.0 (114.1)
H₃COOCH₃	*a*	CO, 1.359 (1.445); OO, 1.391 (1.489); COO, 113.5 (105); COOC, 110.1
(structure: O¹, O², O³ anhydride ring)	*kk*	C¹O¹, 1.201 (1.195); C¹O², 1.366 (1.394); C¹C², 1.504; C²C³, 1.347 (1.330); CH, 1.100 (1.109); HC¹C², 127.4 (129.3); C¹C²C³, 108.9 (107.7); O¹C¹C², 129.8 (129.3)
(structure: epoxide, H₂C—CH₂ with O)	*ll*	CC, 1.447 (1.470); CO, 1.389 (1.435); CH, 1.114 (1.083); HCH, 107.4 (116.3)
(structure: cyclopropanone, C¹, H₂C³—CH₂)	*mm*	C¹C², 1.478 (1.475); C²C³, 1.520 (1.575); CO, 1.189 (1.200); CH, 1.105 (1.086); OC¹C², 149.1 (151.2); HCH, 107.9 (114.1)
(structure: furan-type ring with C¹, C², C³, H¹, H², O)	*nn*	C¹C², 1.367 (1.354); C²C³, 1.455 (1.440); CO, 1.343 (1.371); C¹H¹, 1.104 (1.080); C²H², 1.096 (1.080); C¹C²C³, 105.5 (106.1); OC¹C², 110.0 (110.9); H¹C¹C², 135.8 (133.8)
(structure: C¹, C², C³, H¹, H²)		C¹C², 1.443; C²C³, 1.351; CO, 1.198; CH, 1.092; H¹C²C³, 145.1
(structure: C², C³, C¹, C⁴, O¹, O², H's)	*oo*	CO, 1.204 (1.222); C¹C², 1.505 (1.477); C²C³, 1.348 (1.322); CH, 1.107
O₃⁻	*pp*	OO, 1.323 (1.19); OOO, 122.3 (100)
HO⁻	*d*	HO, 0.949 (0.936)
N₂O₄	*d*	NN, 1.513 (1.750); NO, 1.219 (1.180); NNO, 113.7 (133.7)
(structure: O¹—N with O², O³, H)	*d*	NO¹, 1.394 (1.44); NO², 1.219 (1.223); NO³, 1.221 (1.223); O²NO³, 130.1 (137.8); O¹NO², 111.6 (111.1); O¹NO³, 118.3 (111.1); HO¹N, 118.3 (90 ass.)
(structure: H—C—N with H's, O, O)	*d*	CN, 1.453 (1.471); NO, 1.225 (1.229); CH, 1.116 (1.09 ass.) HCN, 113.7 (109.5 ass.); CNO, 114.3 (106.0)
(structure: H¹, H², N—C with O, H³)	*qq*	CN, 1.334 (1.376); CO, 1.207 (1.193); CH³, 1.139 (1.102); NH¹, 1.016 (1.014); NH², 1.016 (1.002); H¹NC, 126.1 (117.2); H²NC, 123.7 (120.5); NCO, 126.6 (123.7)
H₂NNO₂	*rr*	NN, 1.287 (1.427); NO, 1.229 (1.206); ONO, 132.2 (130.2); HNH, 87.0 (115.1)
(structure: oxazole ring, N—N, C, O)	*ss*	NN, 1.322 (1.399); CN, 1.307 (1.297); CO, 1.348 (1.348); CH, 1.113 (1.075); COC, 102.6 (102.0); NCO, 111.4 (113.4); HCO, 115.1 (118.1); CNN, 107.3 (105.6)

Table II (*Continued*)

a Bond length of XY bond in A (=0.1 nm); XYZ bond angle in degrees; dihedral angle WXYZ in degrees. The dihedral angle WXYZ is defined as the clockwise rotation of YZ from WX, as seen in the direction X → Y. *b* P. G. Wilkinson and N. B. Honk, *J. Chem. Phys.*, **24**, 528 (1956). *c* W. S. Bennett and E. K. Plyler, *Can. J. Phys.*, **35**, 1235 (1957). *d* L. E. Sutton, *Chem. Soc., Spec. Publ.* No. **11** (1958); No. **18** (1965). *e* S. H. Bauer, *J. Amer. Chem. Soc.*, **60**, 524 (1938). *f* P. W. Allen and L. E. Sutton, *Acta Crystallogr.*, **3**, 46 (1950). *g* D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **28**, 572 (1958). *h* T. E. Turner, V. C. Fiora, and W. M. Kendrick, *ibid.*, **23**, 1955 (1953). *i* Y. Morino, T. Tijima, and Y. Murata, *Bull. Chem. Soc. Jap.*, **33**, 46 (1960). *j* W. Beamer, *J. Amer. Chem. Soc.*, **70**, 2979 (1948). *k* C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958). *l* C. C. Costain and B. P. Stoicheff, *ibid.*, **30**, 777 (1959). *m* J. K. Tyler, L. F. Thomas, and J. Sheridan, *Proc. Chem. Soc., London*, **155** (1959). *n* Y. S. Li and J. R. Dring, *J. Mol. Struct.*, **16**, 433 (1973). *o* A. P. Cox, L. F. Thomas, and J. Sheridan, *Nature (London)*, **181**, 1000 (1958). *p* C. N. R. Rao, *Diss. Abstr.*, **19**, 968 (1959). *q* J. A. Ibers and D. P. Stevenson, *J. Chem. Phys.*, **28**, 929 (1958). *r* B. Bak, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectrosc.*, **2**, 361 (1958). *s* P. J. Wheatley, *Acta Crystallogr.*, **10**, 182 (1957). *t* B. Bak, D. Christensen, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.*, **24**, 720 (1956). *u* D. G. Lister and J. K. Tyler, *Chem. Commun.*, 152 (1966). *v* W. S. Benedict, N. Gailer, and E. K. Plyler, *J. Chem. Phys.*, **24**, 1139 (1956). *w* O. Bain and P. A. Giguère, *Can. J. Chem.*, **33**, 527 (1955). *x* K. Kimura and M. Kubo, *J. Chem. Phys.*, **30**, 151 (1959). *y* M. Yamaha, *Bull. Chem. Soc. Jap.*, **27**, 170 (1954). *z* R. B. Lawrence and M. W. P. Strandberg, *Phys. Rev.*, **83**, 363 (1951). *aa* R. W. Kilb, C. C. Lin, and E. B. Wlison, Jr., *J. Chem. Phys.*, **26**, 1695 (1957). *bb* G. W. King, *J. Chem. Soc.*, 5054 (1957). *cc* J. D. Swalen and C. C. Costain, *J. Chem. Phys.*, **31**, 1562 (1959). *dd* G. Herzberg and K. N. Rao, *ibid.*, **17**, 1099 (1949). *ee* C.-P. Courtoy, *Ann. Soc. Sci. Bruxelles, Ser. 1*, **73**, 5 (1959). *ff* A. P. Cox, L. F. Thomas, and J. Sheridan, *Spectrochim. Acta*, **15**, 542 (1959). *gg* M. Sugie, T. Fukuyama, and K. Kuchitsu, *J. Mol. Struct.*, **14**, 333 (1972). *hh* W. J. Tabor, *J. Chem. Phys.*, **27**, 974 (1957). *ii* R. F. Curl, Jr., *ibid.*, **30**, 1529 (1959) *jj* L. Leiserowitz and F. Nader, *Angew. Chem., Int. Ed. Engl.*, **11**, 514 (1972). *kk* R. L. Hildebrandt and E. M. A. Peixoto, *J. Mol. Struct.*, **12**, 31 (1972). *ll* T. E. Turner and J. A. Howe, *J. Chem. Phys.*, **24**, 924 (1956). *mm* J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **91**, 1896 (1969). *nn* B. Bak, L. Hansen, and J. Rastrup-Andersen, *Discuss. Faraday Soc.*, **19**, 30 (1955). *oo* O. F. Bizri and F. E. Prichard, *J. Mol. Struct.*, **14**, 75 (1972). *pp* J. M. Sichel, *Can. J. Chem.*, **51**, 2124 (1973) *qq* C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960). *rr* J. K. Tyler, *J. Mol. Spectrosc.*, **11**, 39 (1963). *ss* L. Nygaard, R. L. Hansen, J. T. Nielsen, J. Rastrup-Andersen, G. O. Sorensen, and P. A. Steiner, *J. Mol. Struct.*, **12**, 59 (1972).

Table III. Calculated and Observed Dipole Moments

| Compd | —Dipole moment, D— | |
	Calcd	Obsd*a*
NH_3	1.63	1.47
CH_3NH_2	1.09	1.29
$(CH_3)_2NH$	0.71	1.03
$CH_3CH_2NH_2$	1.27	1.11
⟩NH	1.26	1.89
H_2NNH_2	2.39	1.9
CH_3NHNH_2	1.59	1.69
$CH_3N\equiv NCH_3$ (cis)	1.34	1.4
⟩NH	1.99	1.84
$PhNH_2$	1.34	1.56
HCN	1.62	2.95
CH_3CN	2.04	3.97
O_3	1.37	0.55
H_2O	2.11	1.82
H_2O_2	1.77	2.07
CO	0.49	0.13
CH_3OH	1.48	1.71
Phenol	1.36	1.55
CH_3OCH_3	0.82	1.30
⟩O	1.76	1.89
⟩O	0.20	0.69
CH_2O	2.10	2.34
CH_3CHO	2.83	2.68
$CH_2=C=O$	1.32	1.34
CH_3COCH_3	3.16	2.86
$HCOOCH_3$	1.99	1.77
CH_3CH_2COOH	1.97	1.76
HNO_3	2.38	2.16
CH_3NO_2	3.53	3.46
NH_2CHO	3.87	3.25–3.75
$(CH_3)_2NCHO$	3.40	3.84

a A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.

Apart from obvious applications to the study of organic reactions, MINDO/3 should prove of value in biology and biochemistry. It provides for the first time a procedure that can give reasonable estimates of molecular energies for systems large enough to be of biological interest, and the calculations for such systems can be carried out with complete optimization of the molecular geometry at reasonable cost. Preliminary studies, to test our procedures, have already included calculations for the nucleotide bases and lysergic acid diethylamide (LSD). It should be quite feasible to carry out calculations of reaction paths for systems large enough to duplicate the active sites of enzymes.

References and Notes

(1) Part XXVI: R. C. Bingham, M. J. S. Dewar, and D. H. Lo, preceding paper in the series.
(2) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and the Robert A. Welch Foundation through Grant F-126. The calculations were carried out using the CDC 6400/6600 computer at The University of Texas Computation Center.
(3) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, part XXV of the series.
(4) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262, 1275 (1969).
(5) (a) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970); (b) N. Bodor, M. J. S. Dewar, and D. H. Lo, *ibid.*, **94**, 5296 (1972).
(6) Some values have been quoted from a detailed MINDO/3 study of heterocylic bases and prototopic tautomerism in them: M. J. S. Dewar and P. Weiner, to be published.
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