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A Semi-empirical NDDO Method for All-valence-electron Systems. II. Extension to Compounds Containing Nitrogen and/or Oxygen

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Synopsis. A semi-empirical NDDO method is extended to compounds containing nitrogen and/or oxygen, and is applied to the evaluation of the molecular geometries and excitation energies of the compounds and of the heats of reactions relating to them. The agreement between the calculated and observed values is comparable with that previously attained for hydrocarbons except for the conformations of NH_3 and CH_3NH_2.

In the previous paper,[1] a semi-empirical NDDO method was applied to the evaluation of the molecular geometries and excitation energies of a variety of hydrocarbons, and of the heats of reactions among them. It was shown that the NDDO method gave at the same time well-balanced values of the above three quantities. Here, the method will be extended to compounds containing nitrogen and/or oxygen. In the NDDO procedure, the off-diagonal core matrix element between AO's, μ and ν, on the different atoms,

$$H_{\mu\nu} = \frac{1}{2}S_{\mu\nu}(\beta_\mu+\beta_\nu),$$

and the core repulsion energies between atoms A and B,

$$E_{\text{core}}^{AB} = Z_A Z_B\left\{\frac{b}{R_{AB}^a}+c\right\} \qquad (R_{AB}<R_0),$$

are estimated empirically. The empirical parameters in these formulae were determined in the same way as in the previous paper.[1] The parameters obtained are listed in Tables 1 and 2. The equilibrium geometries, heats of reactions, and excitation energies of compounds containing nitrogen and/or oxygen were calculated using the parameters listed in Tables 1 and 2. They are

Table 1. Values of β_μ (eV)

	1s(H)	2s(C)	2p(C)	2s(N)	2p(N)	2s(O)	2p(O)
β_μ	−7.5	−13.2	−9.3	−22.0	−18.6	−30.0	−27.0

Table 2. Parameters in core-core repulsion formula[a)]

	a	b	R_0
H–H	10.45	0.7436	2.642
H–C	14.00	0.5034	2.779
H–N	14.58	0.5334	2.291
H–O	21.97	0.3346	2.015
C–C	13.16	0.4899	3.621
C–N	13.22	0.5432	3.327
C–O	18.09	0.3811	2.147
N–N	17.65	0.3897	2.332
N–O	15.73	0.4676	2.192
O–O	17.18	0.4429	1.902

a) The core-core repulsion energies calculated from the parameters are in eV.

Table 3. Calculated equilibrium geometries of compounds containing nitrogen and/or oxygen[a)]

Compound	Type	Calcd	Obsd[2,3)]
Water	O–H	0.953	0.957
	HOH	119.8	104.5
Methanol[b)]	O–H	0.960	0.967
	C–O	1.378	1.428
	COH	121.2	107.3
Formaldehyde	C=O	1.204	1.210
	C–H	1.102	1.102
	HCH	114.4	121.1
Formic acid	C–O	1.369	1.343
	C=O	1.213	1.202
	C–H	1.078	1.097
$H-C(=O_1)-O_2-H$	HCO_1	129.2	124.1
	OCO	118.0	124.9
	COH	106.7	106.3
Dimethyl ether[b)]	C–O	1.391	1.42
	COC	125.4	111.0
Ammonia	N–H	1.048	1.014
	HNH	120.0	106.9
Methylamine[b)]	C–N	1.515	1.474
	HNH	117.0	105.8
Hydrazine	N–H	1.077	1.04
	N–N	1.439	1.47
	HNN	117.2	108
Hydrogen cyanide	H–C	1.086	1.066
	C≡N	1.147	1.153
Azomethane[b)]	C–N	1.552	1.482
	N=N	1.219	1.247
	NNC	125.1	112.3
Diazomethane	C–N	1.362	1.34
	N=N	1.121	1.13
	C–H	1.101	
	HCH	111.8	
Acetonitrile	C–C	1.487	1.465
	C≡N	1.166	1.155
Hydroxylamine	N–O	1.412	1.46
	HNH	115.0	107
	NOH	118.5	103
Formamide	C–N	1.360	1.300
	C=O	1.234	1.255
	HNH	114.2	
	NCO	118.1	121.5
Nitromethane[b)]	C–N	1.550	1.47
	N–O	1.236	1.22
	ONO	126.2	135
Ethylene oxide	C–C	1.536	1.472
	C–O	1.438	1.436
	C–H	1.086	1.082
	HCH	114.0	121.7

a) Bond lengths in Å; bond angles in degrees.
b) The geometry of the CH_3 group was assumed to be the same as that of ethane.

Table 4. Calculated heats of reactions (kcal/mol)[a)]

Reaction	Heats of reaction	
	Calcd	Obsd[4)]
$1/2N_2+3/2H_2\rightarrow NH_3$	9.4	11.0
$N_2H_4\rightarrow N_2+2H_2$	17.6	22.7
$HCN+2H_2\rightarrow CH_3NH_2$	49.0	37.9
$CH_2O+H_2\rightarrow CH_3OH$	39.1	20.4
$CH_3CHO+H_2\rightarrow C_2H_5OH$	30.1	16.5
$CH_2CO+H_2\rightarrow CH_3CHO$	30.0	25.2
$CH_2N_2+H_2\rightarrow CH_4+N_2$	69.8	69.2
$CH_3NH_2+O_2\rightarrow CH_3NO_2$	13.7	5.5
$H_2+1/2O_2\rightarrow H_2O$	56.2	57.8
$H_2+O_2\rightarrow H_2O_2$	54.9	32.5
$CH_4+1/2O_2\rightarrow CH_3OH$	51.0	30.2
$CH_2O+1/2O_2\rightarrow HCOOH$	63.3	62.8
$CH_3CHO+1/2O_2\rightarrow CH_3COOH$	69.6	64.0
Ethylene$+1/2O_2\rightarrow$Ethylene oxide	36.0	24.7
$CH_2CO+H_2O\rightarrow CH_3COOH$	43.4	31.4
$CH_3NNCH_3\rightarrow C_2H_6+N_2$	60.2	71.4

a) The energy of the ground state of O_2(triplet) was calculated by means of the CI method.

Table 5. Calculated excitation energies (eV)

Compound	Nature of excitation	Calcd	Obsd[3,5)]
Formaldehyde	$n\rightarrow\pi^*$	3.05	4.2
	$n\rightarrow\sigma^*$	5.80	7.1
	$\pi\rightarrow\pi^*$	7.53	8.0
Acetaldehyde	$n\rightarrow\pi^*$	3.22	3.56
	$\pi\rightarrow\pi^*$	7.63	6.82
Ketene	$n\rightarrow\pi^*$	2.62	3.84
	$\pi\rightarrow\pi^*$	5.69	5.82
Diazomethane	$n\rightarrow\pi^*$	2.14	3.14
	$\pi\rightarrow\pi^*$	5.03	5.70
Nitromethane	$n\rightarrow\pi^*$	3.38	4.59
	$\pi\rightarrow\pi^*$	6.75	6.12

listed in Tables 3—5. All the bond lengths except the CN-type ones agree with the observed values within 0.05 A. The XOY types of bond angles are larger than the observed values by about 15°. The method fails to give the correct conformations of NH_3 and CH_3NH_2; it predicts the planar conformations. These defects were also found in the NINDO/2 method, which is at the same level of parametrization as the present method; the XOY types of bond angles were estimated to be 180° by MINDO/2.[6)] The agreement between the calculated and observed heats of reactions (average error, 9 kcal/mol) is comparable with that previously attained for hydrocarbons. The singlet excitation energies of several compounds were calculated by the CI method, in which only singly excited configurations were included. The calculated energies for the $n\rightarrow\pi^*$ types of excitations are smaller than the observed values about by 1 eV, while those for the $\pi\rightarrow\pi^*$ types differ from the observed values by about 0.5 eV. This somewhat large discrepancy comes from the empirical parameters which were chosen so as to give, at the same time, well-balanced values for the above three quantities. Better excitation energies can be obtained by the use of other sets of parameters which would simultaneously give poor molecular geometries and heats of reactions.[1)] The present NDDO results in Table 5 are felt to be satisfactory in comparison with the excitation energies[7)] estimated by the CNDO and MINDO/2 methods which are currently used in the theoretical studies of chemical reaction processes.

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7) The $n\rightarrow\pi^*$ excitation energy of formaldehyde, for example, calculated by the MINDO/2 was 2.19 eV. See also: O. Kikuchi, *Bull. Chem. Soc. Jpn.*, **42**, 47 (1969).