J. Am. Chem. Soc. **1993,** *115,* 11906–11917

Molecular Mechanics (MM3). Calculations on Nitrogen-Containing Aromatic Heterocycles

Julia C. Tai,[†] Linrong Yang,[‡] and Norman L. Allinger*,[‡]

Contribution from the Department of Natural Sciences, University of Michigan–Dearborn, 4901 Evergreen Road, Dearborn, Michigan 48128, and Computational Center for Molecular Structure and Design, Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556

Received January 19, 1993[●]

Abstract: The MM3 force field has been extended to cover aromatic heterocycles of the pyridine and pyrrole types. Structures (32 compounds), heats of formation (35 compounds), dipole moments (35 compounds), and vibrational spectra (11 compounds) have been examined, and the results are good for structure and fair for the other items.

Introduction

Molecular mechanics has become a powerful tool in recent years for the study of molecular structures and various attendant properties.[1] The MM3 force field[2] has been developed more recently to improve the accuracy and generality of these calculations. Conjugated molecules create special problems in these calculations because the bond lengths and the attendant force constants for the aromatic part of the molecule are not constant and transferable indiscriminately from one molecule to another but need to be determined for individual cases. The procedure,[3] briefly, is to carry out an SCF calculation on the π system of the conjugated molecule and obtain the bond orders of the individual bonds of the aromatic part of the molecule from these calculations. The bond orders are assumed to be linearly related to the force constants for stretching and torsion and to the natural bond lengths (l_o) of the bonds. Having derived these quantities from the SCF calculation, we then carried out a straightforward molecular mechanics calculation. If the molecule changes its geometry significantly, the SCF and molecular mechanics cycles are iteratively repeated until no further change occurs. The calculational scheme works well for conjugated hydrocarbons, including nonplanar systems, as far as structure is concerned.[3] The heats of formation for a variety of aromatic hydrocarbons were also calculated to approximately within experimental accuracy. The vibrational spectra, on the other hand, are calculated less well, with an rms error over a set of standard compounds of about 63 cm^{-1}.

The calculations on the aromatic hydrocarbons show that while the method used here is, in general, satisfactory, the spectroscopic accuracy is not as good as desired. Improvement in this part of the calculation will require additional crossterms, or interaction terms, for interactions of the type stretch–stretch and bend–bend involving vicinal atoms, etc. While it is desirable to improve the spectroscopic calculation, the force field is sufficiently accurate already to give quite good geometries and energies. While we are working independently on the spectroscopic calculations, the present extensions of the MM3 force field are purely extensions to new kinds of geometric systems involving nitrogen and not fundamental additions to the terms in the force field. Nitrogen-containing heterocycles are probably the most important group of heterocycles, with oxygen-containing heterocycles perhaps second and sulfur-containing heterocycles third. We have simultaneously, with this work, carried out a study of oxygen heterocycles, which will be reported separately.[4] Sulfur-containing heterocycles are under examination. This paper is limited to a discussion of heterocycles which contain nitrogen as part of a conjugated or aromatic ring system.

Method

The general method has been described previously in detail for π systems containing carbon atoms.[3] In order to add nitrogen to the conjugated system, it is necessary to add those parameters which explicitly involve the nitrogen. The nitrogens which are found in common aromatic heterocycles are of two types, the pyridine type (atom type number 37) and the pyrrole type (atom type number 40). In addition, type 72 is used for an imine nitrogen which is not part of a conjugated system, and type 107 is used for a nitrogen in a diazene. (A conjugated imine is type 37.) Most parameters are the same for type 37 as they are for type 72, so any parameter not specifically assigned a value for 72 defaults to the 37 value. This information is summarized in Table 1, where also are given all of the additional parameters derived in this work that must be added to the MM3 force field and which involve these types of nitrogens. The following discussion describes the procedure used for the development of these parameters.

π-Orbital Parameters. When heteroatoms were introduced into the conjugated system in MM2, the parameters needed to calculate the π-system energy were developed using the same formulations as those for

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[†] University of Michigan–Dearborn.

[‡] University of Georgia.

[●] Abstract published in *Advance ACS Abstracts,* October 1, 1993.

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0002-7863/93/1515-11906$04.00/0

Table 1.

Torsional Parameters (kcal/mol)

atom types	v_1	v_2	v_3	atom types	v_1	v_2	v_3
1 1 37 2	0.000	0.000	0.000	1 2 2 40	0.000	15.000	0.000
1 2 37 1	0.088	10.000	0.000	2 2 2 40	0.000	14.000	0.000
1 2 37 2	0.000	6.000	0.000	1 2 40 2	0.000	14.000	0.000
2 2 37 1	0.000	10.000	0.000	2 2 40 1	0.000	14.000	0.000
1 2 2 37	0.000	7.500	0.000	2 2 40 2	0.000	14.000	0.000
2 2 2 37	1.000	10.000	0.000	5 1 2 40	0.000	0.000	0.000
2 2 37 2	1.000	15.000	0.000	5 1 40 2	0.000	0.000	0.000
5 1 1 37	−1.000	−1.000	0.000	5 2 2 40	−3.150	3.000	0.000
5 1 2 37	0.000	0.000	0.000	5 2 40 2	0.000	7.000	0.000
5 1 37 2	0.000	0.000	−0.980	1 2 40 23	0.000	14.000	0.000
5 2 37 1	0.000	12.200	0.000	2 2 40 23	−3.150	8.000	0.000
5 2 2 37	0.755	10.000	0.000	5 2 40 23	−0.530	3.000	0.000
5 2 37 2	−6.650	20.000	0.000	2 2 40 37	1.500	15.000	0.000
1 2 37 23	0.000	14.000	0.000	37 2 2 40	−0.900	15.000	0.000
2 2 37 23	0.779	6.000	0.000	40 2 37 2	0.000	10.000	0.000
5 2 37 23	0.000	15.000	0.000	5 2 37 40	0.000	10.000	0.000
37 1 1 37	0.000	0.000	0.000	5 2 40 1	0.000	14.000	0.000
2 2 37 37	0.000	20.000	0.000	5 2 40 37	0.000	15.000	0.000
2 37 37 2	0.000	25.000	0.000	2 37 40 23	0.000	10.000	0.000
37 2 2 37	2.500	7.000	0.000	37 2 40 23	−2.744	15.000	0.000
37 2 37 2	0.000	13.000	0.000	37 2 37 40	2.754	10.000	0.000
5 2 37 37	0.000	14.000	0.000	23 107 107 23	2.800	32.000	0.000
Five-Membered Ring							
2 2 2 37	0.000	15.000	0.000	2 37 40 2	0.000	10.000	0.000
2 2 2 40	0.000	14.000	0.000	37 2 2 40	−0.300	15.000	0.000
2 2 40 2	0.000	14.000	0.000	37 2 40 2	0.000	15.000	0.000
2 2 37 2	0.000	12.000	0.000	40 2 37 2	0.000	10.000	0.000
2 2 37 40	0.000	10.000	0.000	37 2 40 37	0.000	15.000	0.000
2 2 40 37	0.000	15.000	0.000	37 2 37 40	0.000	10.000	0.000

Bond Parameters (md/Å, Å)

atom types	k_s	l_o	μ	s-slope	t-slope	atom types	k_s	l_o	μ	s-slope	t-slope
1 37	5.000	1.434	1.400	0.000	0.000	23 72	5.970	1.019	1.400	0.000	0.000
1 40	4.230	1.490	1.640	0.000	0.000	37 37	9.500	1.250	0.000	7.650	0.220
2 37	9.000	1.271	1.290	8.000	0.185	2 72	9.000	1.270	1.300	0.000	0.000
23 40	6.500	1.050	1.460	0.000	0.000	23 107	5.350	1.033	1.200	0.000	0.000
Five-Membered Ring Stretching Constant											
2 37	10.000	1.258	1.150	8.250	0.238	37 40	9.600	1.220	−0.500	8.000	0.196
2 40	9.700	1.268	0.500	6.300	0.196						

van der Waals Parameters

atom type	element	example	r_v	ϵ	atom type	element	example	r_v	ϵ
23	H	H—N amine/imine	1.600	0.018	72	N	=N imine, oxime (not conj)	1.930	0.043
37	N	N=C/pyridine	1.930	0.043	107	N	N=N/azo (not conj)	1.930	0.043
40	N	Nsp^2 (conj pyrrole)	1.930	0.043					

Bending Parameters

atom types	k_θ	θ_o CR_2	θ_o CHR	θ_o CH_2	atom types	k_θ	θ_o CR_2	θ_o CHR	θ_o CH_2
1 1 37	0.500	110.740	0.000	0.000	37 2 37	1.200	120.000	122.000	0.000
1 2 37	0.720	115.100	121.300	0.000	23 37 37	0.900	106.400	0.000	0.000
1 37 2	0.720	109.000	0.000	0.000	5 1 40	0.360	109.400		
2 2 37	0.970	121.000	121.000	0.000	1 2 40	0.450	120.000	0.000	0.000
2 37 2	1.200	112.600	0.000	0.000	1 40 2	0.490	120.500	0.000	0.000
5 1 37	0.803	107.500	0.000	0.000	2 2 40	0.660	119.000	0.000	0.000
5 2 37	0.530	119.000	121.500	0.000	5 2 40	0.500	110.000	0.000	0.000
2 37 23	0.670	109.800	0.000	0.000	2 40 23	0.490	118.500	0.000	0.000
2 37 37	1.300	107.500	0.000	0.000	23 40 37	0.490	116.000	0.000	0.000
Five-Membered Ring									
2 2 37	0.550	120.000	122.500	0.000	2 37 40	0.430	114.000	0.000	0.000
2 37 2	0.550	118.000	0.000	0.000	2 40 37	0.430	123.000	0.000	0.000
2 2 40	0.550	122.500	120.100	0.000	37 2 40	0.550	124.000	0.000	0.000
Out-of-Plane Bending Parameters									
2 37	0.250				40 2	0.700			
2 40	0.050				40 23	0.050			
40 1	0.050				40 37	0.150			

π-Orbital Parameters

bond type	AETH	ABNZ	CB	DB	EISO (kcal)	ECONJ (kcal)	RISO (Å)	RCONJ (Å)
2–37	2.307	2.161	0.238	0.740	131.9	113.5	1.267	1.339
37–37	2.307	2.161	0.210	0.640	91.3	65.0	1.248	1.307
2–40	2.307	2.161	0.255	0.840	105.0	83.0	1.250	1.350
37–40	2.307	2.161	0.255	0.770	129.37	108.0	1.220	1.320
40–40	2.307	2.161	0.264	0.600	81.35	42.62	1.150	1.331

Table 1 (Continued)

Heat Parameters

bonds		normal	strainless	bonds		normal	strainless
1 37	C—N= conj imine	28.7204	23.3300	23 37	H—N= conj imine	12.2500	9.9900
1 40	N—C pyrrole	11.8100	20.3460	23 40	H-N pyrrole	–0.9771	6.9360
1 72	C—N= imine	11.8100	–3.0350	23 72	H—N= imine	12.2500	–2.3050
2 72	N═C imine	23.9780	39.9750	107 107	N═N azo	7.4421	38.2100
			Delocalized Bonds				
2 37		137.9962	140.5670	2 40		97.6946	101.5220
37 37		96.1002	102.2890	37 40		126.1468	123.4350
			Structural Features				
2-Me	pyrrole	0.5100	–0.0450	1,3-*N*,*N*	(pyrimidine)	7.5109	–0.8290
3-Me	pyrrole	0.2550	–0.0225	1,4-*N*,*N*	(pyrazine)	–0.0393	0.3590
2-Me	pyridine	–2.3908	–2.1240	1,3-*N*,*N*	(imidazole)	7.8326	–1.3820
3-Me	pyridine	0.2583	0.0160	37–2–37	(triazole)	–4.6200	–8.6650
4-Me	pyridine	–0.4213	–0.6800	37–2–2–40	(imidazole)	–4.4931	–4.0800

Resonance Energy Parameters for Kekule Structure

bond	atom type	parameters	bond	atom type	parameters
$C_{sp^2}—C_{sp^2}$	2 2	–96.22	$N_{sp^2}—N_{sp^2}$	37 37	–35.27
$C_{sp^2}═C_{sp^2}$	2 2	–129.01	$N_{sp^2}═N_{sp^2}$	37 37	–89.10
$C_{sp^2}—N_{sp^2}$	2 37	–90.83	$C_{sp^2}–N_{sp^2}$	2 40	–61.27
		Structure Feature			
$C_{sp^2}—N_{sp^2}—C_{sp^2}$	2 40 2 (sec)	–127.38	$C_{sp^2}—N_{sp^2}—C_{sp^2}$	2 40 2 (tert)	19.48

carbon atoms, except for the resonance integral β_{ij} over atomic orbitals i and j when either or both of i and j are heteroatoms.[2m] In MM2, this integral was taken to be proportional to the β_{CC} of a C–C bond of the same length. Although this procedure was simple and gave good structures, it did not give good energies. It was therefore decided to change the procedure for calculating β_{ij} in MM3 to one that would be consistent, regardless of the atom types of i or j. Furthermore, while values of β between nonbonded atoms were, in general, set to zero in MM2, they are all included in MM3. The procedures for calculating both the bonded and nonbonded resonance integrals are described below.

The integral β_{ij} between bonding atoms i and j when both are carbon atoms is calculated by the following equation:[5]

$$\beta_{ij}(R_{ij}) = {}^3/_2[-E_b^{C=C}(R_{ij})_{ethylene} + E_b^{C=C}(R_{ij})_{benzene} - {}^1/_4\gamma_{11} + {}^5/_{18}\gamma_{12} - {}^1/_{36}\gamma_{14}] \quad (1)$$

where $E_b^{C=C}(R_{ij})_{ethylene}$ and $E_b^{C=C}(R_{ij})_{benzene}$ are respectively the bond energies of the ethylene C–C bond and the benzene C–C bond as a function of distance R_{ij}. The bond energy $E_b^{C=C}$ is a Morse-type function given by

$$E_b^{C=C} = E_e^{C=C}[2\exp[-a(R_{ij} - R_e)] - \exp[-2a(R_{ij} - R_e)]] \quad (2)$$

where $E_e^{C=C}$ is the bond energy at the equilibrium distance R_e and a is a constant.

In the MM3 program, the quantities $E_e^{C=C}$, R_e, and a are named EISO, RISO, and AETH, respectively, when associated with ethylene and ECONJ, RCONJ, and ABNZ when associated with benzene. For bonds other than C–C (type 2-2), similar quantities are assigned to each kind of bond. For example, for a C–N (type 2-37) bond, RISO is the equilibrium bond length of a C–N double bond such as that found in methanimine, RCONJ is the equilibrium bond length of a conjugated C–N bond such as that in *s*-triazine, EISO is the bond energy of the C–N double bond, and ECONJ is the energy of the conjugated C–N bond. Values differing from the experimental values were often used to better fit the structure and energy of a group of molecules, and estimated values were used if experimental ones were lacking.

Resonance integrals β_{ij} between nonbonded atoms i and j are calculated differently. This is because eq 1 is not suitable for R values typical of nonbonded distances. According to eq 1, the absolute value of β increases rather than decreases with a distance beyond a certain R value (for the C–C bond, this occurs at about 1.7 Å). Therefore, the value of the nonbonded β is taken to be proportional to the overlap integral S, and the proportionality constant is called CB in the MM3 program. The overlap integral S is a function of the quantity $DBR_{ij}(Z_i + Z_j)$, where the Zs are nuclear charges and DB is a constant which controls the sharpness of the drop of S with distance. In general, CB and DB are chosen such that the nonbonded β vs R curve matches the bonded β vs R curve at about one bond distance. The parameters discussed above were determined and are listed in Table 1 for the types of bonds present in the compounds studied here. In addition, since MM3 uses a variable electronegativity self-consistent field (VESCF) scheme,[2e] equations relating ionization potential and nuclear charge are needed for each atom type. These were previously developed for the two types of nitrogen orbitals involved here.[6] Other π-orbital parameters for the nitrogen atoms are the same as those used in MM2. Nonbonded parameters are from earlier work.[2]

Self-Consistent Field Calculations. There are some unusual features in the SCF calculations in this work which will be discussed here. In the MM3 program, we use a VESCF rather than an SCF sequence, for reasons discussed earlier.[2e] Sometimes, if one starts too far away from the electronic system which is ultimately arrived at after the VESCF calculations converge, the iterations do not converge but diverge. This usually happens because the change in the effective nuclear charge (Z) is too great. Therefore, MM3(92) needs some remedial action in order to get convergence at this point. The required action is usually simple enough. One only needs to do a straight SCF calculation until convergence occurs and then switch over to the VESCF procedure. The converged SCF orbitals and the auxilliary data are sufficiently close to the final values that convergence ordinarily occurs without difficulty. This feature in the program has now been automated, so that MM3(93) and later versions of the program will handle this automatically.

A further difficulty also was observed in these and other heterocyclic systems. In some cases, it was noted that the VESCF calculations converged but they converged by a systematic increase in the energy of the system. Of course, the Variation Principle requires that for a given system, improving the orbitals will lower the energy. However, in the VESCF calculations, one does not have a given system. The whole system changes every iteration because the values for Z on each atom change. Thus, one sometimes observes convergence but in the direction of increasing energy.

The way the program now works is this. After two VESCF iterations, the energies are compared and the absolute value of the change in energy is noted. In the next iteration, as long as the absolute value of the energy difference from the previous iteration is smaller, convergence is occurring, and the calculations are allowed to proceed. The checking is continued at each iteration, and the calculation proceeds until either convergence is reached (the energy change from the last iteration is sufficiently small) or the absolute value of the energy difference increases, which indicates divergence. Should the latter happen, the program automatically switches into the SCF sequence and carries out SCF calculations until convergence

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is obtained there. The data from that calculation are then used as input data for the initial VESCF calculation, and the latter proceeds as previously.

The test of whether or not one has in fact achieved self-consistency in these calculations is, of course, that one can take the orbitals and data from one iteration, do another iteration, and find no change (to within the limits specified, which are quite small). This scheme almost always works, and no special further effort is needed.

Stretching and Bending Parameters. The initial equations relating the bond length and the stretching force constant to the bond order of a type 2-37 bond were determined using the structures and the IR frequencies of methanimine and pyridine. For the type 37-37 bond, the corresponding data from *trans*-diazene and pyridazine were used. Bond angles and bending constants were determined to give optimum structures for the above mentioned molecules plus pyrimidine, pyrazine, pyridazine, triazine, and *s*-tetrazine. The vibrational frequencies were then calculated, and the parameters were modified to improve the fit of the calculated frequencies to experimental ones while keeping the structures the same. When there was a conflict between spectrum and structure, the latter was given more weight. Bending and stretching parameters involving types 40 and 72 nitrogens were determined in a similar manner.

Torsional Parameters. The V_1 and V_3 terms of the torsional parameters about the 2-37 and 2-40 bonds were at first set to zero. When appropriate energy data were available, they were assigned nonzero values as will be discussed later. The V_2s were initially assigned estimated values unless IR spectral data were available. As most of the molecules studied are planar, their structures are insensitive to the V_2 values used. One of the few nonplanar molecules is *N*-benzylideneaniline. It has a large C–C–N–C (2-2-37-2) angle of 50°, the two C–N bonds being between two phenyl rings. The experimental dihedral angle can be roughly reproduced with V_2 of C–C–N–C equal to about 15, considerably larger than the value of 12.0 chosen earlier to best fit IR spectra. We found earlier with the alkenes that we could not fit both rotational barriers and torsional spectra at the same time with only a V_2 term. A V_4 term is also required but is outside the bounds of MM3. The value 15 was chosen primarily to fit the structure.

The conformational energies of 2-propen-1-imine are experimentally known and were used to determine the V_1 values for C–C–C–N and C–C–N–H (2-2-37-23). The difference in energy of *trans*-diazene and *cis*-diazene was used to find the V_1 for 23-107-107-23. Additional V_1 values were assigned to correctly calculate heats of formation.

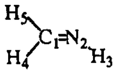
V_3 of 5-1-37-2 was chosen to fit the N–CH_3 barriers of *N*-methylmethanimine and *N*-methylethanimine. V_3 of 5-1-2-37 was chosen to fit the C–CH_3 barriers of *trans*-ethanmine, *cis*-ethanimine, and *N*-methylethanimine.

Heats of Formation. Heats of formation were calculated for all the molecules studied here for which experimental values were available. In addition to the parameters discussed above, bond-energy increments were needed. Structural parameters and modified values for V_1, and sometimes for V_2, and V_3, might also be needed. A least-squares fit of all heat of formation data was carried out to arrive at the best values for these parameters. Experimental data were usually weighted according to their stated precision.

Results and Discussion

Structure. We began with pyridine and then expanded the system to quinoline and isoquinoline, etc. We also expanded the number of nitrogens in the system, from pyridine to pyrazine and pyrimidine, etc. For pyrrole, we extended the calculations to indole and carbazole, etc., and finally to molecules like imidizole and purine which contain both kinds of nitrogen. The calculated structures and the corresponding experimental data are summarized in Tables 2–33.[82] The MM3 force field has been parameterized to fit to r_g-type structures. While good r_g structures are available for a few of the simple molecules of this class, for the most part these molecules are large, and the structures were determined by X-ray crystallography. These structures were usually determined at room temperature, and because of the thermal vibrations of the molecules in the crystal (rigid body motion), the structures usually contain bond-length errors that are quite substantial. Also, X-rays detect the location of electrons not of atomic nuclei, and for an atom such as the pyridine nitrogen, the electron density is not centered at the nucleus. The X-ray location of the atom therefore does not correspond to the location as determined by MM3 or by either the electron diffraction or microwave methods. It is therefore necessary to be more tolerant about fitting the structures with this class of compounds than fitting those with most of the molecules previously studied with MM3. The errors introduced by the comparison of X-ray structures and MM3 structures are of a known order of magnitude and mostly in a known direction, so that systematic discrepancies could be and were approximately taken into account in the comparisons.

Table 2. Structure of Methanimine (bonds in Å and angles in deg)



	experimental[a]	calculated
1–2	1.273	1.276
1–4	1.09	1.104
1–5	1.09	1.102
2–3	1.021	1.021
2–1–4	123.3	122.3
2–1–5	119.7	120.6
4–1–5	116.9	117.2
1–2–3	110.5	111.4
I_a	0.4265	0.4299 (0.8%)
I_b	2.4153	2.4345 (0.8%)
I_c	2.8418	2.8643 (0.8%)

[a] Microwave.[7]

A perusal of Tables 2–33 shows that in general, allowing for the problems with the definition of bond length discussed above, the agreement of the calculated values with the experimental values is good.[82] These data will therefore not be discussed in detail, but we will only comment on a few specific items.

Hydrogen bonding is of minor importance with most compounds discussed here, and it has not been studied in the present work.

Open-Chain Compounds. We first examined methanimine, the structure of which is known from microwave studies (Table 2). *N*-Methylmethanimine and the *Z* and *E* isomers of ethanimine were then fit as well as possible (Tables 3–5). Everything here could be fit very well, except for the C–C–N bond angle in the *Z* and *E* isomers of ethanimine. The problem there is that the angle opens up to a relatively greater extent in going from the *E* to the *Z* isomer than we calculate. We cannot fix this within the context of the present force field but would need to add a torsion–bend interaction to do so. Consequently, the error will have to be left as is for now. The calculated energy difference puts the *E* isomer more stable than the *Z* isomer by 0.26 kcal/

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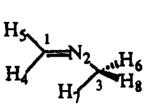
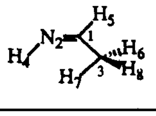
Table 3. Structure of *N*-Methylmethanimine (bonds in Å and angles in deg)



	experimental[a]	calculated
1–2	1.30	1.278
1–4	1.091	1.102
1–5	1.081	1.102
2–3	(1.440)[b]	1.449
3–H	(1.089)[b]	1.119
2–1–4	(120.5)[b]	120.4
2–1–5	(121.5)[b]	122.8
4–1–5	(118.0)[b]	116.9
1–2–3	116.9	117.8
2–3–6	(109.4)[b]	108.8
2–3–7	(109.4)[b]	112.2
2–3–8	(109.4)[b]	108.8
1–2–3–7 = ω		0
I_a	1.59778	1.6069 (0.6%)
I_b	7.86799	7.9372 (0.9%)
I_c	8.94948	8.9889 (0.4%)
$E(\omega = 0)$	0	0
$E(\omega = 180°)$	1.97	1.79

[a] Microwave.[8] [b] Assumed.

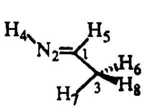
Table 4. Structure of (*Z*)-Ethanimine (bonds in Å and angles in deg)



	experimental[a]	ab initio[b]	calculated
1–2	(1.273)	1.33	1.278
1–3	1.510		1.512
1–5	(1.092)		1.104
2–4	(1.021)	1.020	1.020
3–H	(1.093)		1.115
2–1–3	121	124	125.1
3–1–5	(117.0)		115.2
1–2–4	(110.4)	112.8	111.7
1–3–H	(109.5)		111.5
I_a	1.6797		1.7597 (4.8%)
I_b	8.5388		8.4789 (–0.7%)
I_c	9.7015		9.6956 (–0.6%)
barrier C–Me	1.475	0.6	1.34

[a] Microwave,[9] assumes H—N═C—H geometry as in CH_2–NH. [b] The CH_3CH fragment was assumed to be as in $CH_3CH{=}CH_2$.[10]

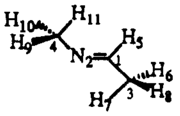
Table 5. Structure of (*E*)-Ethanimine (bonds in Å and angles in deg)



	experimental[a]	semiempirical[b]	calculated
1–2	(1.273)	1.265	1.278
1–3	1.525	1.492	1.509
1–5	(1.092)	1.085	1.106
2–4	(1.021)	1.048	1.021
3–H	(1.093)	1.080	1.115
2–1–3	126	122.5	122.4
2–1–5	117	122.3	121.8
3–1–5	(117.0)	115.2	115.8
1–2–4	(110.4)	112.2	111.3
1–3–H	(109.5)	111.2	111.2
I_a	1.5798		1.5831 (0.2%)
I_b	8.5822		8.7745 (2.2%)
I_c	9.6446		9.8136 (1.8%)
rotnl barrier C–Me	1.595		1.56

[a] Microwave,[9] assumes H—N═C—H geometry as in CH_2–NH and trans more stable. [b] PRDDO[11] (partial retention of diatomic differential overlap calculation).

Table 6. Structure of (*E*)-*N*-Methylethanimine (bonds in Å and angles in deg)



	experimental[a]	ab initio[b]	calculated
1–2	(1.300)	1.248	1.279
1–3	1.50	1.500	1.509
1–5	1.090	1.090	1.104
2–4	1.43	1.443	1.449
3–H	1.089	1.085	1.115
4–H	1.089	1.086	1.112
2–1–3	121.5	122.4	122.1
2–1–5	(120.0)	121.6	122.3
3–1–5	118.5	116.0	115.6
1–2–4	118	118.8	117.8
1–3–H	(109.5)		
2–4–H	(109.5)		
2–1–3–7		0	0
1–2–4–11		0	0
I_a	2.19329		2.2328 (1.8%)
I_b	20.5761		20.8124 (1.1%)
I_c	21.7234		21.9461 (1.0%)
rotnl barrier C–Me	1.64	1.39	1.56
rotnl barrier N–Me	2.11	1.78	1.78

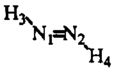
[a] Microwave.[12] [b] 6-31G*.[76]

mol. The experimental values of the rotational barriers for the methyl groups in these molecules and in (*E*)-*N*-methylethanimine are mostly known and they are well calculated (Tables 3–6).

The structures of *cis*- and *trans*-diazene, the parent of the azo compound series, and 2-propen-1-imine were also examined. The trans structure was fit to within satisfactory limits and fixed many of the parameters needed for calculation on open-chain compounds of these types. The cis isomer is reasonably well fit, but the NNH bond angle is a bit small, as discussed for the ethanimines. We chose at this point to separate the conjugated imine nitrogen as type 37 from that which is not conjugated in the simple compounds listed above, which is type 72. Most of the parameters are the same for these two atom types, but by giving them different type numbers, we can distinguish those few parameters which need to be different in order to fit the experimental data. Type 107 was used for the diazene nitrogen, for similar reasons.

Compounds Containing Only Pyridine-Type Nitrogen Atoms. The calculations and the experimental data for these molecules are summarized[82] in Tables 9–23. The π systems of most of the compounds studied are planar, so the geometries offer no information on the values of the torsional constants. Furthermore, there is very little variation in the C–N bond lengths. The open-chain molecules have $R_{CN} \simeq 1.280$ Å, and the monocyclic compounds, aciridine, and phenazine have $R_{CN} \simeq 1.340$ Å. Since it takes only two points to determine a linear equation, our bond order–bond length equation would best be tested and modified by considering molecules with more widely different C–N bond lengths. In this respect, the structure of *N*-benzylideneaniline is useful. It has two C–N bonds between two phenyl rings. Experimental bond lengths for these two bonds are 1.432 and 1.284 Å. The long C–N bond distance is at least 0.05 Å longer than the longest C–N bond distance in any of the other molecules studied. The molecule is also nonplanar, with a dihedral angle C–C–N–C of 50° about the longer C–N bond. These features were all approximately calculated. Other molecules that have or may have nonplanar dihedral angles involving the nitrogen atom are 2,5-diphenylpyrazine (experimental C–C–C–N, 20°), 2,2′-bipyridine (experimental N–C–C–N, 180°, and C–C–C–N, 0°), and 1-(1-naphthyl)isoquinoline (experimental C–C–C–N, 63°). In addition to the stable anti form (N–C–C–N, 180°), 2,2′-bipyridine was found experimentally to have a second stable conformer at a N–C–C–N at 60°, with an energy 2.7 kcal/mol higher than that of the anti form, while the *ab initio* value for

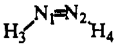
Table 7. Structures of *trans*-Diazene and *cis*-Diazene (bonds in Å and angles in deg)



trans

trans-Diazene

	experimental[a]	calculated
1–2	1.252 ± 0.002	1.253
1–3	1.028 ± 0.005	1.033
1–2–4	106.85 ± 0.47	105.8
I_a	0.2797	0.2806 (0.3%)
I_b	2.1449	2.1527 (0.4%)
I_c	2.4327	2.4333 (0.0%)



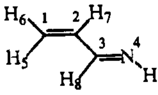
cis

cis-Diazene

	ab initio[b]	calculated
1–2	1.251	1.260
1–3	1.036	1.037
1–2–4	112.3	110.1
$E_{cis} - E_{trans}$	7.2	7.07

[a] Reference 13. [b] Reference 14. Geometry was calculated with double-ζ basis set and self-consistent electron pairs; energy was calculated with triple-ζ and two sets of partially optimized polarization functions for a total of 72 functions.

Table 8. Structure of 2-Propen-1-imine (TA) 2–3–4–9 180° and 1–2–3–4 180° (bonds in Å and angles in deg)



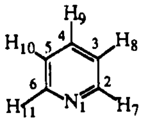
	experimental[a]	calculated
1–2	1.336	1.344
2–3	1.454	1.464
3–4	1.274 ± 0.01	1.284
4–9	1.014 ± 0.01	1.030
1–2–3	122.9	122.6
2–3–4	121.5 ± 1	120.6
3–4–9	111.7 ± 1	111.7
I_a	1.8333	1.8463 (0.6%)
I_b	18.3999	18.5451 (0.8%)
I_c	20.2303	20.3914 (0.8%)

Relative Energy

	TA	TS	CA	CS
experimental[a]	0.0	0.88 ± 0.1	>2.3	>3.7
ab initio[b] (4–31G)	0.0	0.9	1.90	3.66
ab initio[c]	0.0	1.1	1.8	3.8
MM3	0.0	0.88	2.60	3.70

[a] Reference 15. Microwave. [b] Reference 16. [c] Reference 17.

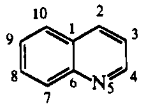
Table 9. Structure of Pyridine (bonds in Å and angles in deg)



	experimental[a]	experimental[b]	calculated
1–2	1.3376	1.344	1.3474
2–3	1.3938	1.399	1.3960
2–7	1.0865	1.096	1.1033
3–4	1.3916	1.398	1.3901
3–8	1.0826	1.092	1.1029
4–9	1.0818	1.094	1.1026
2–1–6	116.94	116.1	117.25
1–2–3	123.80	124.6	123.04
1–2–7	116.01	115.2	117.49
2–3–4	118.53	117.8	119.38
2–3–8	120.12	119.3	120.35
3–4–5	118.40	119.1	117.90
3–4–9	120.80	120.5	121.05
I_a	13.8983		13.9540 (0.4%)
I_b	14.4594		14.5215 (0.4%)
I_c	28.3641		28.4756 (0.4%)

[a] Reference 18. r_s structure. [b] Reference 19. r_g, by combined analysis of ED, MW, IR, and *ab initio*.

Table 15. Structure of Quinoline (bonds in Å and angles in deg)



	experimental[a]	*ab initio*[b]	calculated
1–2	1.418	1.425	1.422
1–6	1.424	1.404	1.410
1–10	1.418	1.429	1.428
2–3	1.358	1.377	1.367
3–4	1.403	1.419	1.422
4–5	1.321	1.318	1.320
5–6	1.378	1.366	1.384
7–8	1.371	1.378	1.374
8–9	1.417	1.424	1.422
9–10	1.362	1.376	1.374
2–1–6	117.8		118.8
2–1–10	123.4		121.7
1–2–3	119.8		118.3
2–3–4	118.5		119.8
3–4–5	125.0		123.4
4–5–6	117.2		117.8
1–6–5	121.8		122.0
1–6–7	119.9		119.1
6–7–8	119.0		120.6
7–8–9	121.3		120.3
8–9–10	120.4		120.3
1–10–9	120.6		120.3

[a] Reference 27. For corresponding bonds and angles in 8,8-biquinolyl, X-ray. [b] Reference 28.

the angle is 40–43°.[32] (Our calculation showed a second conformer at a N–C–C–N at 27°, 4.0 kcal/mol higher in energy than the anti form.)

Molecules Containing Pyrrole-Type Nitrogens. The structures of nine molecules containing pyrrole-type nitrogens were studied, and the results are summarized in Tables 24–33. Good experimental structures are available only for pyrrole, imidazole, and pyrazole. They were relied upon heavily in deriving the parameters. The calculated structures for these and the other compounds are quite good except for purine. For purine, although most bond lengths were fit to within 0.01 Å of the experimental values, two of the five bonds in the imidazole ring were calculated to be too long by 0.02 Å, while the structure of imidazole itself was very well calculated. The experimental purine structure is from an old X-ray study. Because of the presence of the purine ring in many biologically important molecules, this problem will be further investigated.

The structure of another molecule, porphine, which is the parent of a biologically important class of molecules was also calculated. Porphine has four pyrrole rings connected at the α carbon by CH chains forming a large ring with four nitrogen atoms pointing toward the center of the ring. Two hydrogen atoms are attached to two opposing nitrogen atoms, which are of the pyrrole-type. The other two nitrogens do not have hydrogens attached and are of the pyridine-type. We calculated the structure of this compound by treating the first two nitrogen atoms as type 40 and the other

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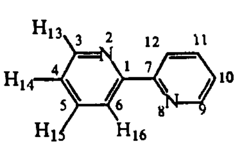
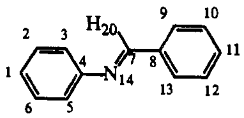
Table 18. Structure of 2,2'-Bipyridine (bonds in Å and angles in deg)



	experimental[a]	experimental[b]	calculated
1–2	1.349	1.352	1.356
1–6	1.408	1.389	1.404
1–7	1.500	1.498	1.482
2–3	1.365	1.352	1.344
3–4	1.368	1.389	1.395
3–13	1.045	1.105	1.103
4–5	1.373	1.389	1.388
4–14	1.124	1.105	1.103
5–6	1.396	1.389	1.389
5–15	1.083	1.105	1.103
6–16	1.041	1.105	1.102
2–1–6	122.5	122.8	121.2
2–1–7	118.8	116.1	118.6
1–2–3	116.7	116.6	118.3
2–3–4	124.3	124.3	123.1
2–3–13	117.3	116.1	117.5
3–4–5	118.6	117.6	119.1
3–4–14	122.7	121.2	120.5
4–5–6	119.7	118.5	118.1
4–5–15	119.4	120.6	121.0
1–6–5	118.3	120.7	120.2
5–6–16	119.5	117.8	119.3
2–1–7–8	180.0		180.0

[a] Reference 31. X-ray, $R = 0.15$. Error <0.025 Å in any bond length. [b] Reference 32. Electron diffraction.

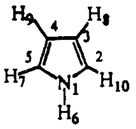
Table 19. Structure of *N*-Benzylideneaniline (bonds in Å and angles in deg)



	experimental[a]	experimental[b]	calculated
1–2	1.371	assumed	1.396
1–6	1.395	planar ring	1.395
2–3	1.406	R(C–C) = 1.398 ± 0.005	1.396
3–4	1.386		1.406
4–5	1.375	R(C–H) = 1.095 ± 0.010	1.401
5–6	1.398		1.395
4–14	1.460	1.432 ± 0.015	1.441
7–8	1.496	1.440 ± 0.015	1.471
7–14	1.237	1.284 ± 0.010	1.293
8–9	1.380		1.404
8–13	1.391		1.406
9–10	1.406		1.396
10–11	1.364		1.395
11–12	1.380		1.397
12–13	1.405		1.394
3–4–14	123.7	122.7 ± 2	123.2
5–4–14	117.3		117.9
8–7–14	122.7	125.0 ± 1.5	121.0
14–7–20		118 (117–123)	120.8
7–8–9		120.0 ± 1.5	120.2
4–14–7	119.8	115.0 ± 2.0	119.4
3–4–14–7	–56.9	52 ± 5	–27.4
13–8–7–14	–9.9	0 ± 15	–1.0

[a] Reference 33. X-ray, $R = 4.9\%$. [b] Reference 34. Electron diffraction.

Table 24. Structure of Pyrrole (bonds in Å and angles in deg)



	experimental[a]	calculated
1–2	1.370	1.380
2–3	1.382	1.382
3–4	1.417	1.417
1–6	0.996	1.052
2–10	1.076	1.098
3–8	1.077	1.100
2–1–5	109.8	110.1
1–2–3	107.7	107.1
2–3–4	107.4	107.8
1–2–7	121.5	121.7
2–1–6	125.1	125.0
4–3–8	127.1	126.1
3–2–7	130.73	131.2
I_a	9.19558	9.2477 (0.6%)
I_b	9.32764	9.3870 (0.6%)
I_c	18.52599	18.6348 (0.6%)

[a] Reference 40.

two as type 37. The calculated structure and the X-ray structure reported by Chen and Tulinsky[51] are shown in Table 33. To within experimental error, the two pyrrole-type rings are identical but different from the other two, which are also identical to each other, in the crystal structure and also in NMR studies.[84] Thus, there is a C_2 axis running through the two N–H bonds. In fact, the molecule in the crystal appears to have D_{2h} symmetry, slightly deformed by crystal lattice forces. The experimental bond lengths and angles are reported in Table 33, averaged over D_2 symmetry, and these are compared with the average bond lengths and angles calculated by MM3. The SCF calculation of the large cyclic polyene 18-annulene gave alternating bond lengths at that level, but these were equalized when electron correlation was included.[72] The experimental (X-ray) structure contained (approximately)

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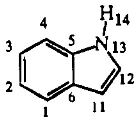
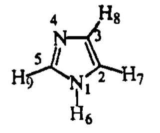
Table 25. Structure of Indole (bonds in Å and angles in deg)



	experimental[a]			
	A	B	experimental[b]	calculated
1–2	1.386	1.390	1.382	1.382
1–6	1.410	1.388	1.425	1.414
2–3	1.394	1.399		1.427
3–4	1.403	1.382	1.382	1.382
4–5	1.398	1.407	1.425	1.414
5–6	1.408	1.404	1.382	1.402
5–13	1.391	1.402	1.370	1.383
6–11	1.401	1.401		1.431
11–12	1.399	1.407	1.382	1.378
12–13	1.392	1.406	1.370	1.392
2–1–6	120.3	120.6	117.2	118.2
1–2–3	120.2	119.8		121.0
2–3–4	120.1	120.5		121.0
3–4–5	120.2	119.8	117.2	118.2
4–5–6	119.6	119.8	121.4	120.9
4–5–13	132.3			131.7
6–5–13	108.1	107.9	108.7	107.4
1–6–5	119.6	119.7	121.4	120.7
5–6–11	107.8	108.4		107.4
6–11–12	107.8	108.4		107.6
11–12–13	108.7	108.0	109.1	108.2
5–13–12	107.9	108.1	109.1	109.5
I_a			21.6387	21.6966 (0.3%)
I_b			51.2889	51.6570 (0.7%)
I_c			72.9091	73.3536 (0.6%)

[a] Reference 41. Disordered crystal structure with the indole molecule capable of assuming two alternative orientations. Gross structure R = 0.23, structure A 0.66 weight, structure B 0.33. [b] Reference 83, microwave.

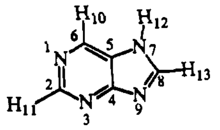
Table 27. Structure of Imidazole (bonds in Å and angles in deg)



	experimental[a]	experimental[b]	calculated
1–2	1.378	1.381	1.375
1–5	1.355	1.358	1.366
1–6	1.064	1.053	1.051
2–3	1.369	1.378	1.377
2–7	1.091	1.087	1.096
3–4	1.382	1.389	1.382
3–8	1.084	1.086	1.100
4–5	1.333	1.333	1.328
5–9	1.088	1.087	1.098
2–1–5	106.9	107.2	107.7
2–1–6	126.0	125.7	126.0
1–2–3	106.3	106.0	105.0
1–2–7	123.7	123.0	122.8
2–3–4	109.8	109.8	111.0
2–3–8	128.2	128.0	125.5
3–4–5	105.1	105.3	104.7
1–5–4	111.8	111.8	111.6
1–5–9	123.9	123.7	120.8

[a] Reference 43. Neutron diffraction at –150 °C, R = 0.074. [b] Reference 44. Neutron diffraction at –173 °C.

Table 29. Structure of Purine (bonds in Å and angles in deg)



	experimental[a]	calculated
1–6	1.330 (1.336)	1.327
5–6	1.393 (1.385)	1.399
6–10	1.00 (0.93)	1.101
1–2	1.349 (1.349)	1.379
2–3	1.339 (1.324)	1.331
2–11	1.06 (0.97)	1.103
3–4	1.337 (1.336)	1.351
4–5	1.407 (1.398)	1.391
4–9	1.379 (1.369)	1.399
5–7	1.373 (1.375)	1.378
7–8	1.327 (1.337)	1.378
7–12	0.89 (0.84)	1.050
8–9	1.311 (1.313)	1.320
8–13	0.95 (1.06)	1.098
1–6–5	118.9 (119.0)	119.0
1–6–10	118.7 (113.9)	119.6
2–1–6	118.4 (117.5)	118.0
1–2–3	128.5 (127.9)	126.8
1–2–11	121.9 (114.4)	116.6
2–3–4	113.0 (113.4)	114.6
3–4–5	123.9 (123.1)	122.4
5–4–9	109.6 (109.6)	110.3
4–5–6	117.9 (118.5)	119.2
4–5–7	105.1 (105.5)	105.5
5–7–8	106.5 (106.3)	107.0
5–7–12	118.8 (126.6)	126.4
7–8–9	115.1 (114.1)	112.6
7–8–13	123.1 (120.3)	120.3
4–9–8	103.8 (104.6)	104.6

[a] Reference 46. Two independent investigations. R = 0.070, σ = 0.001 Å, and 0.8° (W); R = 0.048, σ = 0.006 Å, and 0.6° (SM) (values in parentheses). The molecules are joined together by relatively short (2.85 Å, N(7)H···N(9)) hydrogen bonds.

equal bond lengths, and these were shown not to result from disorder in the crystal. The same situation probably applies here. Our calculation is at the SCF level without correlation, and the bond lengths alternate (while the crystal bond lengths do not, as fas as can be told). Thus, the SCF calculation dictates two separate structures of C_2 symmetry, which could be valence tautomers but are probably just resonance forms. The D_2 structure results from averaging them. If there are actually two tautomers, the barrier between them is quite low and they are interconverting rapidly (compared to the time scale of the X-ray[51] and NMR[84] experiments). Hence, the X-ray structure is the average of the two. If, in fact, electron correlation stabilizes the resonance hybrid more than it does the individual valence tautomers, which would be analogous to the 18-annulene case, then again we will get an average structure. That the latter is probably the correct interpretation is supported by the fact that the thermal motion parameters observed in the X-ray study are no larger for the atoms which are required to move in this valence tautomerization than for atoms which are not required to move. Thus, there is no disorder from the mixing of tautomers. Consequently, in Table 33, we compare the D_2-averaged structures for the calculated and observed molecules. If we average the structures corresponding to the two Kekule forms, we get the values in Table 33, which should compare with the experimental values. Since the latter are artificially shortened by thermal motion, we actually expect our calculated values to be longer by 0.005–0.010 Å or so, and in general, this is what is found. Averaging the Kekule forms for the most part makes the long bonds shorter and the short bonds longer. The exceptions are the bonds which are

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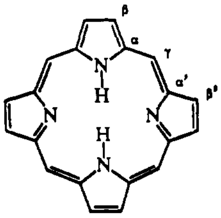
Table 33. Structure of Porphine (bonds in Å and angles in deg)



	experimental^a		calculated	
	average	range	average	range
C_α–N	1.380	1.377–1.383	1.387	1.378–1.396
C_α–C_β	1.430	1.425–1.437	1.434	1.398–1.470
C_β–C_β	1.365	1.359–1.371	1.383	1.359–1.406
C_α–C_γ	1.387	1.378–1.398	1.404	1.362–1.449
$C_{\alpha'}$–N	1.377	1.363–1.389	1.377	1.312–1.443
$C_{\alpha'}$–$C_{\beta'}$	1.452	1.439–1.465	1.459	1.455–1.463
$C_{\beta'}$–$C_{\beta'}$	1.345	1.344–1.346	1.348	1.348–1.348
$C_{\alpha'}$–C_γ	1.376	1.373–1.382	1.404	1.359–1.449
C_β–C_α–N	107.9	106.9–108.6	107.0	106.9–107.2
C_α–N–C_α	108.6	107.8–109.3	110.0	109.7–110.2
C_α–C_β–C_β	107.8	107.4–108.2	108.1	107.8–108.3
N–C_α–C_γ	125.2	124.8–125.8	127.0	126.9–127.2
C_α–C_γ–$C_{\alpha'}$	127.1	126.5–127.7	125.0	124.9–125.1
$C_{\alpha'}$–N–$C_{\alpha'}$	106.1	105.9–106.3	106.7	106.7–106.7
$C_{\alpha'}$–$C_{\beta'}$–$C_{\beta'}$	107.2	106.1–108.4	107.2	106.4–108.0

[a] Reference 51. X-ray.

Table 34. Heats of Formation (kcal/mol)

wt	compound	expt^a	calc	Δ
5	*N*-methylmethanimine	18.53	18.53	0.00
5	*trans*-diazene	36.00^b	36.00	0.00
10	pyridine	33.55	33.60	0.05
10	2-methyl	23.71	23.91	0.20
10	3-methyl	25.43	25.47	0.04
9	4-methyl	24.88	24.77	–0.11
9	2,3-dimethyl	16.32	16.13	–0.19
9	2,4-dimethyl	15.27	15.07	–0.20
9	2,5-dimethyl	15.89	15.77	–0.12
8	2,6-dimethyl	14.03	14.20	0.17
9	3,4-dimethyl	16.75	17.06	0.31
5	3,5-dimethyl	17.40	17.34	–0.06
8	pyrimidine	46.82	46.82	0.00
8	pyrazine	46.87	46.96	0.09
9	pyridazine	66.52	66.52	0.00
0	quinoline	51.8^d	49.24	–2.56
0	isoquinoline	48.2^d	49.94	1.74
7	quinoxaline	62.70^e	62.44	–0.26
1	*N*-benzylideneaniline	60.60	61.06	0.45
4	dibenzylidene-1,2-ethylenediamine	84.87	84.87	0.00
1	acridine	69.90^e	68.96	–0.94
1	phenazine	82.17	82.46	0.29
0	3,4-benzoquinoline	58.20	64.04	5.84
0	5,6-benzoquinoline	55.90	64.04	8.14
0	7,8-benzoquinoline	55.19	63.93	8.89
1	pyrrole	25.88	24.99	–0.92
1	*N*-methylpyrrole	24.64	24.64	0.00
1	2,5-dimethylpyrrole	9.51	9.51	0.00
1	indole	37.41	38.56	1.16
1	carbazole	50.10	49.92	–0.18
1	imidazole	32.34^c	32.03	–0.31
1	benzimidazole	45.79^c	46.10	0.31
1	pyrazole	41.56^c	42.91	1.35
1	indazole	59.39^c	58.04	–1.35
1	1,2,4-triazole	46.07^c	46.07	0.00
			rms =	0.50

[a] Unless specified, ΔH_f values are taken from ref 52. [b] Reference 53. [c] From ref 53, converted from heats of atomization in ref 54. [d] Reference 71. [e] Reference 86.

marked β′–β′, which are short in both Kekule forms, and those marked α′-β′, which are long in both Kekule forms. Table 33 shows that the β′–β′ bond is the shortest carbon–carbon bond in the molecule, both by calculation and by experiment, while the α′–β′ bond is the longest. This is consistent with the NMR data as well.

In principle, there exists another tautomer of porphine, which differs from the common one in that the hydrogens attached to nitrogen are on adjacent rings rather than on transannular rings. This tautomer has never been observed experimentally. MM3 calculations show why. Because of unfavorable van der Waals repulsions between the two hydrogens plus unfavorable electrostatics and various distortions introduced from the van der Waals repulsions and electrostatics, this tautomer is calculated to be higher in energy than the standard one by 8.20 kcal/mol. It is most unusual from the viewpoint of the calculations in that it has C_s symmetry, with the plane of the molecule being the symmetry plane. It has one vibrational frequency exactly equal to 0 cm^{-1}, however. This means that in an effort to avoid each other, the two hydrogens on nitrogen can move simultaneously in opposite directions perpendicular to the symmetry plane. In this motion, each hydrogen drags the five-membered ring to which it is attached along with it, so the rings wave up and down in a concerted fashion. The very high energy of this interesting tautomer makes it unlikely that it will ever be observed directly, but it might be possible to prepare substituted derivatives.

Heats of Formation. Heats of formation are important properties of molecules, and it has previously been shown that they can be well calculated using MM3[2] for hydrocarbons, conjugated or unconjugated. It is similarly possible to calculate rather well the heats of formation of the oxygen heterocycles.[4] For the nitrogen heterocycles, the results are somewhat mixed. For the most part, the heats of formation can be calculated adequately, but there are a significant number of exceptions. It is not known whether the discrepancies here are due mainly to experimental or to calculational error.

The heats of formation of 34 compounds were calculated and are presented in Table 34 together with the experimental values. It can be seen that the deviations in most cases are less than 1 kcal/mol. The heats of formation of the three benzoquinolines were calculated too high by 6–9 kcal/mol. Since these molecules contain no unusual structural features but are very similar to acridine and quinoline, etc., it is difficult to explain this discrepancy, and experimental error seems likely. Accordingly they were not weighted in the heat of formation parameterization. *Ab initio* methods for the calculation of heats of formation are under development, but they are still some distance from being able to deal with molecules such as those discussed here.[75]

It should be noted that structural parameters (environmental) were used to arrive at the calculated heats of formation of some methylpyridines and 2,5-dimethylpyrrole. When a methyl (or alkyl) group is at the 2-, 3-, or 4-position relative to a pyridine nitrogen, –2.3908, 0.2583, or –0.4213 kcal/mol, respectively, should be added. A methyl group at C-2 or C-4 puts σ electron density on to the attached π carbon, from which π density can be relayed to the more electronegative nitrogen. Thus, we can understand the stabilizing effect of the methyl being at C-2 or C-4 but not at C-3. When there is a methyl group at the 2-position relative to the pyrrole nitrogen, 0.5100 kcal/mol should be added (no experimental value is available for the 3-position). In pyrrole, the nitrogen donates π electron density into the π system. The addition of the electron-donating methyl group into either an α or a β position should therefore be unfavorable and lead to an increase in energy, as is observed for the α case. The α parameter was established by fitting the heat of formation of 2-methylpyrrole. Rather than leave the 3-methyl value at zero, it was arbitrarily assigned a value of one-half of that of the 2-methyl. It should also be noted that a few of the molecules in Table 34 have a

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unique feature, and hence, they are fit exactly (*N*-methylmethanimine, *trans*-diazene, pyrimidine, *N*-benzylideneaniline, and the methylpyrroles).

The conformational energies of 2-propen-1-imine were calculated (see Table 8). The calculated values agree with reported *ab initio* calculations.[16,17] The calculated methyl rotational barriers of *N*-methylmethanimine, the cis and trans ethanimines, and (*E*)-*N*-methylethanimine also agree well with the experimental values (Tables 3–6).

Resonance Energies. The idea here historically was a simple one, to try to understand the relative unreactivity of benzene and related compounds compared with that of open-chain polyenes. Resonance energies can be defined and measured in various ways, including the thermodynamic one above, the original definition. A more proper way of interpreting the unreactivity of benzene is to look at the difference in energy between a ground state and a transition state so that resonance energy is only part of the story. Or, more recently, resonance energies have been defined in terms of ring currents as determined from NMR spectra. They may also be defined in various other ways, and not all of these definitions yield the same conclusions.

The MM3 program,[3c] like the MM2 program,[79] utilizes thermodynamic stabilities, specifically heats of formation, to measure resonance energies, following the proposals originally by Dewar[77] and Breslow.[78] This definition picks simple derivatives as having zero resonance energies (butadiene, in the case of polyenes and benzonoid compounds). On this basis, benzene is found to have a resonance energy of 17.8 kcal/mol in MM3, compared with the value of 20.0 kcal/mol found by Dewar from hand calculations. This is purely a thermodynamic quantity and may or may not correlate with such things as ring currents from NMR. However, the quantity has been found to be of some use in understanding certain chemical and physical properties of molecules, and so we will examine it here.

In the case of nitrogen-containing heterocycles, it is necessary to decide what reference compound or compounds will be taken as having zero values for their resonance energies, the values for polyenes already having been fixed.[3c,85]

Table 35. Resonance Energies

compound	resonance energy (kcal/mol)
benzene	17.79
pyridine	17.02
pyridazine	14.35[a]
pyrazine	17.01
pyrimidine	15.60
s-triazine	13.51
s-tetrazine	17.72
naphthalene	26.30
quinoline	25.53
quinoxaline	25.57
isoquinoline	25.68
2,3-diazanaphthalene	20.75[a]
acridine	30.09
phenazine	29.74
pyrrole	26.06
indole	31.28
carbazole	38.75
imidazole	26.07
benzimidazole	30.90
3,4-benzoquinoline	37.57
5,6-benzoquinoline	37.06
7,8-benzoquinoline	37.06
porphine	28.90

[a] Calculated relative to the most stable Kekule form.

It turns out that one needs three values for nitrogen compounds (and looking ahead, two values each for oxygen- and sulfur-containing compounds). In the case of polyenes, the reference compound (butadiene) is defined by its Kekule form, and it has two short bonds and one long bond in the conjugated system. Each of these bonds is assigned an energy, so that when added, the three numbers for the three bonds add to the heat of formation of the Kekule form of butadiene. The resonance energy is the energy of the actual molecule minus that of the Kekule form and is chosen to be zero in butadiene (or in hexatriene or in other linear polyenes). The Kekule form for benzene is determined by inspection to have three long and three short bonds, and the same difference gives benzene a resonance energy of 17.8 kcal/mol. In this case, a positive resonance energy is indicative of stabilization (the heat of formation is more negative than that of the reference compound).

For nitrogen heterocycles, one needs to add into the scheme numbers that depend upon type 37 (pyridine nitrogen) and type 40 (pyrrole nitrogen). For the pyridine nitrogen, there will necessarily be a double bond and a single bond attached to nitrogen in the uncharged Kekule form. We therefore have one parameter, which is for one bond of each type at the same time. In the pyrrole case, the parent compound is vinylamine. The C–N bond is a single bond in the Kekule form of this compound. One can also have an imine-type structure, as in methanimine, where the carbon–nitrogen bond is now a double bond. Hence, we need a parameter for each of these bond types.

But, it turns out that in fact we need additional parameters. We want divinylamine and trivinylamine also to have zero resonance energies because they are the simplest examples of their class. But this means we have to introduce additional parameters, one where the nitrogen is bound to two unsaturated carbons and another where it is bound to three unsaturated carbons.

After introducing these parameters, we can calculate in a clear well-defined way the resonance energies for nitrogen heterocycles. There are, however, two more stipulations which have to be made. First, it is not appropriate to calculate resonance energies for congested molecules, such as 2,3-di-*tert*-butylpyridine. In a molecule like this, the π system is distorted (and its energy raised) because of steric effects, and these really do not directly have to do with the resonance energy of the system we are examining. Additionally, if the system is nonplanar, the resonance energy is not really defined. Again, the π system is distorted as a result

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(85) It has always been our custom to avoid changes in the program even though improvements can always be made. The reason for this is that it would be impossible subsequently to reproduce earlier results. Occasionally exceptions have to be made to correct errors. The calculation for aromatic hydrocarbons is correct to the best of our knowledge with MM3(91). When this calculation was expanded to include heterocycles, a square root sign was inadvertently left out for nonbonded resonance integrals. Since these are small, the parameterization pretty much takes care of the error. However, in MM3-(92), there are slightly inaccurate results (typically 0.001 Å in bond length and 0.2° in bond angle, but perhaps as much as 0.3 kcal/mol in energies). This has all be corrected now in MM3(93), but it is noted that MM3(92) gives slightly inaccurate results with conjugated systems because of this error. The resonance energy calculations were also slightly revised, so that the numbers in this paper, and subsequent numbers, will not agree exactly (but they are quite close) to those given by earlier versions of the program. We regret this inconvenience to the user. We also note that when optimizations are done with the block-diagonal Newton–Raphson method, there may be small differences in geometry and energy (similar to the numbers above) as a result of incomplete minimization. Once the minimization is complete with the block-diagonal method, it is recommended that the full-matrix Newton–Raphson method be applied. The user is warned that if the full Newton–Raphson method is applied to an incompletely minimized geometry, the optimization is only done once, with the original SCF orbitals. If these are not of sufficient accuracy, then a true minimum is not reached. Accordingly, the minimization should be carried out as outlined above.

Table 36. Dipole Moments (debye units)

	expt	calc	Δ	ref[a]
methanimine	2.29	1.92	–0.37	57
	2.02			58
N-methylmethanimine	1.53	1.77	0.24	8
	2.08			58
ethanimine, *Z*	2.45	2.20	–0.25	9
	2.56			11
ethanimine, *E*	2.06	1.91	–0.15	9
	2.32			11
N-methylethanimine	1.50	1.75	0.25	12
2-propenimine (TA)	2.51	2.30	–0.21	15
pyridine	2.25	2.27	0.02	
	2.215			59
2-methyl	1.96	2.08	0.12	
3-methyl	2.40	2.41	0.01	
4-methyl	2.57	2.56	–0.01	
2,3-dimethyl	2.20	2.25	0.05	
2,4-dimethyl	2.30	2.37	0.07	
2,5-dimethyl	2.15	2.20	0.05	
2,6-dimethyl	1.65	1.86	0.21	
3,4-dimethyl	1.87	2.69	0.82	
3,5-dimethyl	2.58	2.53	–0.05	
pyrimidine	2.44	2.36	–0.08	20
	2.334			
pyridazine, in benzene	3.94–4.09	3.85	–0.09	
quinoline	2.22	2.23	0.01	60
isoquinoline	2.75	2.30	–0.45	
	2.53			
3-methylisoquinoline	2.10	2.10	0.00	29
N-benzylideneaniline	1.58	2.06	0.48	
acridine	1.94	2.23	0.29	
pyrrole	1.74	1.75	0.01	40
	1.84			
N-methyl	1.92	1.93	0.01	
2-methyl	1.89	1.78	–0.11	
2,4-dimethyl	1.75	1.66	–0.09	
2,5-dimethyl	2.08	1.88	–0.20	
indole	2.07	1.65	–0.42	
carbazole	2.10	1.41	–0.69	
imidazole	3.87	3.85	–0.02	
benzimidazole	3.96	3.64	–0.32	
purine	4.32	4.39	0.07	61
pyrazole	2.21	2.21	0.00	62
1,2,4-triazole	2.72	2.77	0.05	62
		avg =	–0.02	
		rms =	0.27	

[a] Unless specified, dipole moment values are taken from ref 56.

Table 37. Vibrational Frequencies of Methanimine

sym	no.	mode	expt[65] (cm^{-1})	calc	Δ
A′	1	NH stretch	3264	3262	–2
	2	CH stretch	3038	3006	–32
	3	CH stretch	2915	2918	3
	4	C=N stretch	1638	1722	84
	5	CH_2 scissor	1452	1396	–56
	6	HCNH defor	1344	1308	–36
	7	HCNH defor	1055	1100	45
A″	8	torsion	1173	1135	–38
	9	H_2CN OPLA	1059	1061	2
				rms =	42

Table 38. Vibrational Frequencies of *N*-Methylmethanimine

type	sym	vib no.	expt[a] (cm^{-1})	expt[b]	calc	Δ*b*
CH_2 asym stretch	A′	1	3005	3009	3014	5
CH_3 asym stretch	A′	2	2930	2940	2929	–11
CH_2 sym stretch	A′	3	2894	2896	2912	16
CH_3 sym stretch	A′	4	2768	2774	2811	37
C=N stretch	A′	5	1658	1657	1734	77
CH_2 scissor	A′	6	1467	1477	1480	3
CH_3 asym defor	A′	7	1472	1485	1427	–58
CH_3 sym defor	A′	8	1399	1401	1385	–16
				1407		
CH_2 rocking	A′	9	1218	1223	1336	113
				1234		
CH_3 wagging	A′	10	1098	1194	1082	–112
				1108		
C—N stretch	A′	11	938	939	928	–11
			948	954		
C=N—C	A′	12	400	400	421	21
CH_3 asym stretch	A″	13	2957	2957	2912	–45
CH_3 asym defor	A″	4	1439	1439	1426	–13
CH_3 wagging	A″	15	1045	1049	1082	33
CH_2 rocking	A″	16	1023	1062	992	–70
CH_2 twist	A″	17	478	501	545	44
				497		
CH_3 twist	A″	18	205	205	199	–6
					rms =	51

[a] Reference 64. In argon matrix. [b] Reference 64. Solid state.

of extraneous interactions. Therefore, our resonance energy scheme requires that the calculation be carried out on the planar molecule (whether or not in fact the actual molecule is planar), and it really applies to the parent, not to the substituted molecules. In practice, we have applied it to methyl derivatives, which are probably the same as the parent molecule to within the accuracy of the usefulness of this approximation.

The numbers calculated are shown in Table 35. We note that pyridine has a calculated resonance energy of 17.0 kcal/mol, quite similar to that of benzene. Pyrrole has a resonance energy of 26.1 kcal/mol, quite a bit more than benzene. Other numbers in the table such as those for indole and carbazole show values about as would be expected, considering what the numbers are for benzene and pyrrole. Then a value for porphine is 28.9 kcal/mol. This number is presumed to be too low. The neglect of electron correlation gives a structure which corresponds more nearly to a Kekule form than to the averaged structure, and a more proper treatment which included correlation would presumably lower the heat of formation for porphine and hence raise its resonance energy. Such a calculation is, however, beyond the scope of MM3.

Dipole Moments. The treatment of dipole moments is straightforward for systems which are not conjugated. Bonds are assigned permanent dipole moments, and these are vectorally added to give the resultant molecular dipole moment. Electrostatic energies are calculated by the dipole–dipole interactions (plus additionally charge–dipole interactions and charge–charge interactions if net charges are present). The dipole moment is calculated by summing all of the bond moments in the molecule, whereas the electrostatic energy is calculated only from dipoles that are not bound to a common atom. For the simple unconjugated compounds, bond moments were picked to fit C—N (types 1-72), C=N (types 2-72), and N—H (types 23-72). These numbers were chosen so as to fit the observed moments for methanimine, the ethanimines, *N*-methylmethanimine, and (*E*)-*N*-methylethanimine. This procedure does not give highly accurate results because, in reality, the permanent moments create induced dipoles in neighboring bonds and properly these need to also be added in the calculation. This procedure has been explored,[55] and when the induced moments are included, the general agreement between the experimental and calculated dipole moments is of the order of 0.2 D. When these induced moments are neglected as here, the agreement is often no better than 0.5 D.

For conjugated systems, in general there will be π charges. These make a π contribution to the dipole moment. Hence, the π and σ dipole moments are separately calculated, the latter by the usual scheme used in unconjugated molecules, as described above. The π moments are calculated from the Mulliken charges and the geometry. The two are then summed vectorally to give the molecular dipole moment. Bond moments for bonds involving atoms of type 37 and type 40 were chosen to fit the available experimental data (Table 36). In the more than 30 molecules studied here, the π systems are quite polarizable and the presence of heteroatoms causes significant shifts in electron density, which in turn result in significant variations in dipole moments. The

Table 42. Vibrational Frequencies of Pyridine (cm^{-1})

MM3	exp	sym	assignment (vib no.)	expt[a]	calc	Δ(calc − a)
1	1	A1	CH stretching (2)	3094	3063	−31
3	2	A1	CH stretching (13)	3073	3051	−22
5	3	A1	CH ip bending (20*a*)	3030	3043	13
7	4	A1	ring stretching (8*a*)	1584	1658	74
9	5	A1	ring stretching (19*a*)	1483	1497	14
13	6	A1	ring stretching (9*a*)	1218	1191	−28
17	7	A1	ring stretching (18*a*)	1072	991	−81
18	8	A1	ring stretching (12)	1032	966	−67
19	9	A1	ring breathing (1)	991	891	−100
25	10	A1	ring oop bending (6*a*)	601	593	−8
15	11	A2	CH oop bending (17*a*)	996	1055	59
21	12	A2	CH oop bending (10*a*)	871	813	−58
27	13	A2	ring oop bending (16*a*)	373	371	−2
14	14	B2	CH oop bending (5)	1007	1112	105
20	15	B2	CH oop bending (10*b*)	937	901	−36
22	16	B2	ring oop bending (4)	744	655	−89
23	17	B2	CH oop bending (11)	700	645	−55
26	18	B2	ring oop bending (16*b*)	403	398	−5
2	19	B1	CH stretching (7*b*)	3087	3055	−32
4	20	B1	CH ip bending (20*b*)	3042	3043	1
6	21	B1	ring stretching (8*b*)	1580	1671	91
8	22	B1	ring stretching (19*b*)	1442	1582	140
10	23	B1	ring stretching (14)	1362	1401	39
11	24	B1	Ch ip bending (3)	1227	1297	70
12	25	B1	ring stretching (15)	1143	1205	62
16	26	B1	CH ip bending (18a)	1079	1006	−73
24	27	B1	ring ip bending (6*b*)	652	614	−38
					rms =	62

[a] Reference 69.

calculated and experimental values are summarized in Table 36. The agreement is better than that with MM2, where only a SCF and not a VESCF procedure is used for the π system. As can be seen from the table, the (signed) average deviation is only 0.02 D and the rms deviation is 0.3 D. Except for the cases of *N*-methylmethanimine and (*E*)-*N*-methylethanimine which were discussed earlier, the two major discrepancies occur in the cases of indole and carbazole, the moments for both of which are underestimated by about 0.5 D. The agreement is as good as can be expected.

The MM3 dipole moment of 4.39 D for purine given in Table 36 is the average of the dipole moments of the 7(H) tautomer and the 9(H) tautomer, which are calculated to be 5.50 and 3.28 D, respectively, and these latter two values individually agree well with theoretical calculations.[61] Although the calculated average moment agrees well with the experimental value of 4.32 D measured in dioxane, the relative energies of the two tautomers are not known. In crystals, purine assumes the N(7)H tautomeric form;[46] however, UV absorption studies indicate that the N(9)H form is more stable in aqueous solution, and NMR studies in Me_2SO indicate that the tautomers occur in appproximately equal quantities.[63] A UV photoelectron study concludes that in an isolated environment, the N(9)H tautomer is more stable.[64] We did not attempt to fit the relative energies of the 7(H) and 9(H) tautomers to any specific value, since the proper value is uncertain. The MM3 force field gives the tautomers the same energy.

Vibrational Spectra. A good force field will, of course, enable one to calculate the vibrational spectra of molecules, in addition to the properties mentioned above. In the present work we have carried out vibrational calculations for the following molecules: methanimine, (*Z*)-ethanimine, (*E*)-ethanimine, *trans*-diazene, *N*-methyl-methanimine, pyridine, pyrimidine, pyrazine, pyridazine, *s*-triazine, and pyrrole. The calculated and experimental spectra are presented in Tables 37–47. The average rms error over these compounds (199 frequencies total) is 63 cm^{-1}. This is certainly not a very satisfactory value but is similar to what was obtained with aromatic hydrocarbons and other planar systems. Much of the error comes from the omission of explicit cross terms, especially the 2-center bend–bend interactions. These omissions have a somewhat larger effect upon the overall results here than that which was found with saturated molecules (35 cm^{-1}), and the effect is similar to that found for unsaturated hydrocarbons (46 cm^{-1}). While we recognize the need for improvement in the spectroscopic calulations and are currently working on that problem, we belive the present force field is adequate for calculating molecular structures and other non-spectroscopic properties for molecules of this class.

Table 47. Vibrational Frequencies of Pyrrole (cm^{-1})

sym	no.	mode	expt[62]	calc	calc − exp
A1	1	NH stretch	3410	3409	−1
	2	CH stretch	3132	3120	−12
	3	CH stretch	3108	3096	−12
	4	ring stret	1466	1526	60
	5	ring stret	1384	1365	−19
	6	CH def ip	(1140)[a]	1053	
	7	CH def ip	1076	1022	−54
	8	ring stret	(986)[a]	912	
	9	ring def ip	(893)[a]	711	
A2	10	CH def oop	868	1106	238
	11	CH def oop	(728)[a]	724	
	12	ring def oop	(613)[a]	492	
B1	13	CH stretch	3133	3118	−15
	14	CH stretch	3108	3088	−20
	15	ring stret	1418	1436	18
	16	NH def ip	1146	1198	52
	17	ring stret	1531	1521	−10
	18	CH def ip	1047	1030	−17
	19	CH def ip	1015	971	−44
	20	ring def ip	652	714	62
B2	21	CH def oop	1047	1025	−22
	22	CH def oop	768	806	36
	23	ring def oop	649	539	−110
	24	NH def oop	561	464	−97
				rms dev	71

[a] Numbers in parentheses are the corresponding numbers for furan.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Additional tables (as listed in ref 82) showing calculated and experimental structural and spectral data for the compounds discussed here and input/output data for the calculations (26 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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