

J-CAMD 109

## $\pi$ -SCF-Molecular Mechanics PIMM: Formulation, parameters, applications

Arturo E. Smith and Hans J. Lindner\*

*Institut für Organische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 22, D-6100 Darmstadt, Germany*

Received 6 April 1990

Accepted 12 July 1990

*Key words:* Heat of formation; Molecular geometry; Charge density distribution

---

### SUMMARY

A  $\pi$ -SCF/Molecular Mechanics method (PIMM) for the calculation of heats of formation, molecular geometries and charge density distributions of organic molecules is described. The method combines a  $\pi$ -SCF molecular orbital calculation and the  $\sigma$ -charge evaluation procedure PEOE of Marsilli and Gasteiger with molecular mechanics. The formulas and parameters used are given. A series of results for small molecules is presented and compared with experimental data.

---

### 1 INTRODUCTION

The prediction of molecular conformations and the estimation of heats of formation and charge density distributions in organic molecules has a long tradition in theoretical chemistry. Besides qualitative empirical models familiar to every chemist [1], powerful tools have been developed on the basis of quantum theory [2] at different levels of accuracy, or classical mechanics [3] by setting up empirical force fields. The latter may give ground-state molecular structures as well as molecular heats of formation with good accuracy. However, up till now, the only access to correct representations of electronic systems is provided by quantum mechanics, including relativistic effects for highest accuracy [4].

Gradually increasing the number of nuclei and electrons (N) to be treated explicitly in bonded systems is always accompanied by an  $N^4$ – $N^5$  increase in computational requirements like memory size and processing time. Keeping the performance at the highest levels of accuracy will let the requirements grow quickly beyond the possibilities of any computation system. This is the only founded argument that can be stressed by investigators who introduce approximations or simpli-

---

\* To whom correspondence should be addressed.

fications of existing models, in order to make systems of higher complexity accessible to quantitative computations. The accuracy drops while going over to larger systems, introducing each time new or more drastic simplifications. The merits of a new computational method, extending the numerous family of existing models, should be:

- *to reduce the computational requirements while maintaining the level of accuracy, allowing computations on larger systems to be run without growing expenses, or*
- *to increase the accuracy within a range of applications, allowing the distinction of subtle variations in molecular properties without cutting down the size of the systems under consideration.*

The development of strict methodologies in quantum mechanics, however, does not eliminate or make superfluous the need of empirical models for rapid and reliable estimations of molecular properties and, with the break-through of computer-assisted molecular modeling [5], growing interest is also given to compilations of basic data for known molecular systems as a guideline for the construction of more complex models.

Our early attempts to describe the structure and bonding of strained hydrocarbons led to a theoretical procedure which combined a  $\pi$ -SCF method with molecular mechanics [6]. Thereafter, the same procedure was used in calculations on conjugated hydrocarbons [7], as well as on systems containing heteroatoms [8]. With the inclusion of  $\sigma$ -polarization by the PEOE method of Gasteiger and Marsilli [9], the charge density distribution of a given molecule could finally be approximated by a point charge model. With this background, we developed the program system PIMM,  $\pi$ -SCF/Molecular Mechanics [10], for the computation of heats of formation, geometries and charge density distributions for a large range of organic compounds. Another program system (MOMO) by Egert and Beck [11] makes use of the formulations presented here.

In this publication, we gather the equations and parameters used by PIMM. The method comprehends

- $\pi$ -SCF calculation at the PPP level [12],
- $\sigma$ -charge estimation following Marsilli and Gasteiger [9], and
- molecular mechanics [6].

The coupling of the  $\sigma$  and  $\pi$  electronic charge density distributions and their influence upon the equilibrium positions of the nuclei are formulated. The overall effects of the routines concerning the electronic system and optimization of geometry are simultaneously adjusted to give a balanced model. Calculations on small representative organic molecules are carried out in order to test the method and define the frame within which it should be used. Comparisons with experiment are done for the computed molecular properties.

## 2 PIMM

### 2.1 Mathematical formulation

#### 2.1.1 The $\pi$ -SCF procedure

In the MO model for  $\pi$ -electrons we expand the molecular orbitals  $\Phi_i$  as a linear combination of atomic orbitals  $\varphi_m$  (LCAO approach [13])

$$|\Phi_i\rangle = \sum_m C_{im} |\varphi_m\rangle \quad (1)$$

The summation runs over the total number  $M$  of functions. We then write Schrödinger's equation with an effective Hamiltonian, the Fock-operator [13]

$$h^F |\Phi_i\rangle = e_i |\Phi_i\rangle \quad (2)$$

The  $C_{im}$  are determined by the variation of the total energy, the  $e_i$  (i.e. orbital energies according to Koopmans) are the Lagrange multipliers taking care of the orthogonality of the one-electron wave functions (orbitals). This is done by solving the homogeneous set of simultaneous equations,

$$\sum_m C_{im} (F_{mn} - e_i S_{mn}) = 0 \quad \text{where} \quad n = 1, 2, 3, \dots M \quad (3)$$

$$F_{mn} = \langle \Phi_m | h^F \Phi_n \rangle \equiv \int \Phi_m h^F \Phi_n d\tau \quad \text{with} \quad d\tau = dx dy dz \quad (4)$$

$F_{mn}$  being the elements of the operator  $h^F$  in the matrix representation of the basis in use. The overlap matrix  $S$  is set to identity in the ZDO [14] or zero differential overlap scheme

$$S_{mn} = \langle \Phi_m | \Phi_n \rangle \equiv \int \Phi_m \Phi_n d\tau = \delta_{mn} \quad (5)$$

$\delta_{mn}$  is Kronecker's delta. The equations (3) and (4) may be solved only if

$$\det |F_{mn} - e_i S_{mn}| = 0 \quad (6)$$

The solutions are the eigenvectors and eigenvalues of  $h^F$ . The existing approximative or semiempirical methods differ in the setting up of the Fock matrix or in the choice of the basis set for the expansion of the molecular orbitals (see Eq. (1)). We define Fock's energy matrix  $F_{mn}$  with the one- and two-center contributions  $I_m$ ,  $G_{mm}$  and  $\beta_{mn}$ ,  $G_{mn}$ ,  $G_{ml}$  as follows

$$F_{mm} = -I_m + (1/2 P_{mm} - (q_m^\sigma - q_m^{\sigma^\circ})) G_{mm} - \sum_{n \neq m} (q_n^\pi + q_n^\sigma) G_{mn} - \sum_l (q_l^\sigma + q_l^{\sigma^\circ}) G_{ml} \quad (7)$$

$$F_{mn} = \beta_{mn} - (1/2 P_{mn} - q_m^\sigma q_n^\sigma) G_{mn} \quad (8)$$

We consider the backpolarisation due to the  $\sigma$ -electrons in both diagonal and off-diagonal elements; the first sum in Eq. (7) runs over all centres  $n$  belonging to the  $\pi$ -system, the second recollects the effects of  $\sigma$ -electrons on centres  $l$  outside of the  $\pi$ -system. Our notation reads:

$I_m$  Ionisation energy of the atom  $m$  in the given valence state; the numerical values for  $I_m$  and  $A_m$  in Eq. (11) were taken from the spectroscopic work of Hinze and Jaffé [15].

$P_{mn}$ ,  $P_{mm}$   $\pi$ -Bond order between atoms  $m$  and  $n$  or charge density on  $m$  over all occupied molecular orbitals  $\Phi_i$

$$P_{mn} = 2 \sum_i C_{im} C_{in} \quad \text{and} \quad P_{mm} = 2 \sum_i C_{im}^2 \quad (9)$$

$q_m^\pi, q_m^\sigma$  Net charges. For the  $\pi$ -system we obtain

$$q_m^\pi = N_m - P_{mm} \quad (10)$$

$N_m$  is the number of  $\pi$ -electrons contributed by atom  $m$ . The computation of the net charges for the sigma skeleton will be described in Section 2.1.2.

$q_m^\sigma$  Damping factor for the backpolarisation due to the  $\sigma$ -charge density in the  $\pi$ -electronic system. It is used to balance the correlation of the density distribution in both subsystems.  $q_m^\sigma$  can also be interpreted as the standard density of the corresponding atom.

$G_{mm}$  Repulsion energy for electrons located at the same atom. Following Parr and Snyder [16], we express  $G_{mm}$  as the difference between the ionization energy  $I_m$  and the electron affinity  $A_m$

$$G_{mm} = I_m - A_m \quad (11)$$

$G_{mn}$  Repulsion energy for electrons located at different atoms  $m, n$ . These two-centre contributions are estimated from the one centre energies according to Ohno [17]

$$G_{mn} = e^2 (r_{mn}^2 + 1/4(e^2/G_{mm} + e^2/G_{nn})^2)^{-1/2} \quad (12)$$

$e$  is the elementary charge and  $r_{mn}$  the interatomic distance.

$G_{ml}^\sigma$  For centres  $l$  not belonging to the  $\pi$ -system, the Coulomb potential is used as two-centre ( $\sigma$ ) contribution

$$G_{ml}^\sigma = e^2/r_{ml} \quad (13)$$

$\beta_{mn}$  Resonance integrals. We take them to be proportional to the overlap integrals  $S_{mn}$  (Mulliken [18]), which are calculated numerically

$$\beta_{mn} = k_{mn} S_{mn} = k_{mn} \langle \Phi_m | \Phi_n \rangle = k_{mn} \int \Phi_m \Phi_n d\tau \quad (14)$$

The integral runs over the Cartesian coordinates:  $d\tau = dx dy dz$ . Our basis functions  $\Phi_m$  are Slater type orbitals, STO [19], centred at the nuclei

$$\Phi_m = N \exp \{(-Z_{eff}/2) r\} r \cos \theta \quad (15)$$

$r \cos \theta$  corresponds to the Cartesian  $z$ -coordinate ( $r$  and  $\theta$  are polar coordinates with the nucleus at the origin).  $N$  is a normalizing factor to accomplish  $\langle \Phi_m | \Phi_m \rangle = 1$ :

$$N = \pi^{-1/2} (Z_{eff}/2)^{5/2} \quad (16)$$

$Z_{eff}$  is the effective core charge obtained by the Slater rules [19]. We consider an additional screening arising from the  $\sigma$ -charge density on the particular atom, and also depending on the one-centre integrals  $G_{mm}$  and  $I_m$  [20, 21]:

$$Z_{eff} = Z_{eff}(\text{Slater}) (1 + (q_m^\sigma - q_m^{\sigma^*}) G_{mm}/I_m)^{1/2} \quad (17)$$

The expansion coefficients  $C_{im}$  in Eq. (1) are needed to construct the density matrix  $P$  which appears in the definition of the elements of the Fock matrix (see Eqs. (7) and (8)). This makes it necessary to solve the equations (3) and (6) by the iterative SCF or self-consistent field procedure. The first trial of the SCF matrix is set up by a Hückel MO calculation, with standard parameters for heteroatoms [22].

With theoretical approaches of the present category, introducing spectroscopic data and adjustable parameters in place of the integrals which must be solved at the higher ab initio levels, universal applicability is lost due to the crude simplifications done. Therefore, one should restrict the use of such semi-empirical models to the fields for which they were developed. Nevertheless, computer time requirements are some orders of magnitude lower than those for ab initio calculations. In our treatment of the  $\pi$ -electron system, we need only to compute the resonance integrals  $\beta_{mn}$  and carry out a matrix diagonalization in order to find the eigenvalues and eigenvectors of the SCF matrix in each cycle. Both are standard procedures in modern computer technology [23].

### 2.1.2 The $\sigma$ -polarization

For the computation of the density distribution of  $\sigma$ -electrons, we had two models under consideration:

- the LCAO-MO procedure of Del Re [24], and
- the PEOE method of Gasteiger and Marsilli [9].

Both methods deliver electron density distributions, which change with topology (bonding matrix) but not with molecular geometry (space coordinates of nuclei). Equal results are computed for saturated systems with *syn-gauche-anti*-rotation isomerism.

Del Re postulates a system of simultaneous equations following the spirit of the HMO theory by using only adjustable parameters. The net charge on an atom results from the sum of its respective bond polarizations. The complexity of the model grows quickly when going over to larger systems. Furthermore, the available set of parameters from the literature is still incomplete.

Our decision in favour of Gasteiger and Marsilli's method is based on its direct derivation from experimental facts in combination with rapid convergence without regard to the size of the system under study. The method is based on the assumption of a partial equalization of orbital electronegativities (PEOE) as a consequence of the formation of chemical bonds:

*The difference in electronegativity of neighbouring orbitals on covalently bonded atoms governs the displacements of charge density in the  $\sigma$ -skeleton of a molecule; the strive for equalization is the driving force for the electron density moving away from electropositive sites towards the more electronegative centres.*

Mulliken's definition [25] of electronegativity is used

$$\chi_m = 1/2(I_m + A_m) \quad (18)$$

where  $m$  stands for the valence orbital.  $I_m$  and  $A_m$  are the same spectroscopic energy values for the ionization potential and electron affinity used in the preceding section. This definition (18) of electronegativity instead of the customary one of Pauling [26], allows the development of mathematical relations to give quantitative charge distributions for the  $\sigma$ -skeleton in any molecule.

Let the electronegativity  $\chi_m$  be a power series of the net charge

$$\chi_m = a + bQ_m + cQ_m^2 + \dots \quad (19)$$

Using Eq. (18) together with the promotion energies [15] for ionic valence states with  $Q_m = \pm 1, \pm 2, \dots$ , enables us to find the coefficients  $a, b, c, \dots$  for different atoms in different states of hybridization. The power series (19) is cut off after the square term.

Now the inverse effect of electronegativity on charge density distribution must be clarified. Setting up a system of equations, one per covalent bond, makes a rapid and quantitative computation of the overall charge density distribution possible.

These equations (20) and (21) establish that

- charge displacements between covalently bonded atoms  $m, n$  are proportional to the difference  $(\chi_m - \chi_n)$  in their electronegativities,
- the electronegativity  $\chi_+$  of the more electropositive atom in its valence state with a single formal charge is taken as a scaling factor for the charge displacement, and
- a damping factor  $(1/2)^k$  is introduced to avoid the total equalization of the electronegativities of all atoms in the molecule,  $k$  being the index of the iteration count

$$\delta q_{m,n}(k) = |(1/2)^k (\chi_m - \chi_n)/\chi_+| \quad m, n \text{ bonded} \quad (20)$$

where  $\delta q_{m,n}$  is the absolute amount of the charge displacement taking place between  $m$  and  $n$ . For the more electronegative atom, whose  $\chi$  is more positive,  $\delta q$  is negative, whereas for its bonding partner  $\delta q$  becomes positive

$$\begin{aligned} \delta q_m &= -\delta q_{m,n}(\chi_m - \chi_n) / |(\chi_m - \chi_n)| \\ \text{and } \delta q_n &= -\delta q_m \end{aligned} \quad (21)$$

The equations (19)–(21) are solved by iteration, setting all starting charges to zero. After the  $k$ -th step, the  $Q_m(k-1)$  are updated by adding the respective  $\delta q_m(k)$  values to each atom:

$$q_m^\sigma(k) = q_m^\sigma(k-1) + \sum \delta q_m(k) \quad (22)$$

These charges give rise to new electronegativities for the next step  $(k+1)$ . The damping factor  $(1/2)^k$  guaranties constant values after 10 cycles.

In this work, we consider a bond angle dependence (Eq. 23) of orbital electronegativities, distinguishing between strain-free and highly strained centres, making the latter more electronegative:

$$\chi'_m = \chi_m(1. + 0.03333\Omega_m/\chi_m) \quad (23)$$

$\Omega_m$ , the sum of absolute deviations from the equilibrium bond angle at  $m$ , is updated and delivered by the force field section. Moreover, the net charges  $q_m^\pi$  from the SCF calculation are used to compute the electronegativities  $\chi_m^\circ$  (see Eq. (19)) before entering the PEOE procedure:

$$\chi_m^\circ = a + bq_m^\pi + c(q_m^\pi)^2 \quad (24)$$

In this way we take account of backpolarization of the  $\sigma$ -electrons due to the density distribution of the  $\pi$ -electrons.

The numerical values for  $a$ ,  $b$ ,  $c$  and  $\chi_+$  were taken from the original work [9], except that for the hydrogenic  $\chi_+$ , which can not be derived from experiment because of the nonexistent ionization energy of  $H^+$ . We assume  $\chi_+$  (hydrogen) = 15.00 eV (20.02 eV [9]).

### 2.1.3 The force field

From a chemical point of view, the forces opposing the deformation of bond lengths and angles, torsion and bend angles, together with electrostatic and van der Waals potentials, build up the force field of a molecule. The prior knowledge of these forces as a function of the positions of atoms in space leads to the molecular geometries belonging to energy minima. These structures, in turn, are meaningful in contemplating ground states.

By splitting the energy of deformation and defining its individual terms, we seek to reproduce the structural features of simple molecules and to predict more complex events such as ring inversion in cyclic systems or the geometry of transition states for larger molecules or their associations.

**2.1.3.1 Bond lengths.** For small deviations from the equilibrium bond length,  $r_{ij}^\circ$ , we obtain the strain energy  $E_r^{ij}$  by a harmonic potential

$$E_r^{ij} = 1/2 k_r^{ij} (r_{ij} - r_{ij}^\circ)^2 \quad (25)$$

$$r_{ij}^\circ = a - b P_{ij} \quad (26)$$

$$r^\circ(C \equiv N) = r^\circ(C = N) - 0.120 \text{ \AA} \quad (27)$$

In the range  $0 \leq P_{ij} \leq 2$ , a linear bond length –  $\pi$ -bond order dependence (Eq. 26) has been observed [27]. We add 0.015 Å when the central bond carries four substituents. For saturated single bonds,  $r_{ij}^\circ$  remains constant. The C = N equilibrium bond length is shortened to give the C  $\equiv$  N length in a cyano group (Eq. 27). The force constant  $k_r$  is developed as a power series of the actual distances  $r_{ij}$  [28]:

$$k_r^{ij} = a r_{ij}^{-2} + b r_{ij}^{-4} + c r_{ij}^{-6} \quad (28)$$

For all X–H bonds,  $k_r$  is set to 7 mdyn/Å.

**2.1.3.2 Bond angles.** For bond angles  $\alpha_{k-i-j}$  we also use a harmonic potential

$$E_\alpha^{kij} = 1/2 k_\alpha(i) (\alpha_{k-i-j} - \alpha_i^\circ)^2 \quad (29)$$

The equilibrium bond angle  $\alpha_i$  is treated as an atomic (one-centre) constant. For small carbocycles (3- and 4-membered rings) an additional term is considered.

$$E'_\alpha(3-, 4\text{-ring}) = E_\alpha + 1/2 k'_\alpha (\alpha - \alpha^\circ)^4 \quad (30)$$

For saturated chains X–C (sp<sup>3</sup>)–Y, a widening of the equilibrium bond length to 113° is postulated (not for the previously mentioned small rings).

For nitrogen,  $\alpha^\circ$  changes linearly with the  $\pi$ -charge density  $P_{ii}$  on going from  $sp^2$  to  $sp^3$  hybridization.

$$\alpha_N^\circ(\text{amine}) = 120^\circ - 100^\circ (P_{ii} - 1.90) \quad \alpha^\circ \leq 120^\circ \quad (31)$$

For computational reasons, to avoid linearity, the equilibrium angle at the carbon atom of a cyano group is set to  $177^\circ$ .

**2.1.3.3 Torsional angles.** The barrier to rotation about a bond  $i - j$  and its periodicity are given by the potential (Eq. 32) for torsional angles.  $\tau(k - i - j - l)$  is the angle between the projection vectors  $(i, k)$  and  $(j, l)$  on the plane perpendicular to the bond  $i - j$ . With  $1 - \cos(2\tau)$  for the expression in brackets ([ ]), we get a twofold symmetry for  $\pi$ -bonds with minima at  $0^\circ$  and  $180^\circ$ , while  $1 + \cos(3\tau)$  delivers the threefold symmetry of  $\sigma$ -bonds with minima at  $60^\circ$ ,  $180^\circ$  and  $300^\circ$ :

$$E_\tau^{k-i-j-l} = 1/2k_{kl}[1 \pm \cos(n\tau)] \quad (32)$$

In  $\pi$ -systems an additional term (Eq. 33) accounts for the strength of the central  $\pi$ -bond  $i - j$  through the bond order  $P_{ij}$

$$E_\tau^\pi = E_\tau + k'_{kl}(P_{ij} + 0.15P_{ij}^2 + k_{ij}\sin^2\tau)\sin^2\tau \quad (33)$$

**2.1.3.4 Bend angles at  $sp^2$  centres.** Deviations from planarity at central  $\pi$ -atoms  $i$  with three bonding partners  $j, k$  and  $l$  give rise to the potential (Eq. 34), where  $\tau'$  is the angle between the vector  $(i, l)$  and the plane  $(j, i, k)$ .

$$E_\tau(i) = 1/2k_i\tau'^2 \quad (34)$$

$$E_\tau(N) = 0.001(2. - P_{ii})\tau'^2 \quad (35)$$

For this contribution, again a linear dependence on the  $\pi$ -SCF charge density  $P_{ii}$  on amine nitrogens (Eq. 35) is postulated.

**2.1.3.5 Electrostatic potential.** The  $\sigma - \sigma$ ,  $\pi - \sigma$  and  $\pi - \pi$  interactions between electron densities on different centres are characterized by the Coulomb potential

$$E_Q^{mn} = (q_m^\sigma + q_m^\pi)(q_n^\sigma + q_n^\pi)/(e_r r_{mn}) \quad (36)$$

The dielectric constant  $e_r = 1.0$  is used for calculations on isolated molecules. A distance variable dielectric can be defined

$$e_r = r^n \quad n = 0, 1, 2, \dots \quad (37)$$

for complexes or associations of molecules. In this case, the exponent  $n$  for the relation (Eq. 37) is declared in the input and  $e_r$  is used for intra- and intermolecular interactions. This variable dielectric allows the simulation of solvent effects and a proper description of intermolecular electrostatics during optimization of geometry, especially for molecular associations. Warshel and Levitt [29] have also proposed to define different regions with different dielectric constants within the system, but doubt has been expressed about similar procedures [30].



**2.1.3.6 Van der Waals interaction.** The representation of nonbonding interactions is crucial in force-field definitions [31]. We use the relation of Giglio [32], which was parameterized to reproduce experimental lattice energies and interatomic distances in molecular crystals

$$E_{vdW} = a \exp\{-br\}/r^d - c/r^6 \quad (38)$$

The original work [32] did not include the electrostatic forces explicitly, making a redetermination of the constants  $a$ – $d$  necessary.

**2.1.3.7 Coordinated metal cations.** Metal-ligand equilibrium distances and coordination energies are computed using only the described nonbonding (electrostatic and van der Waals) potentials. With the van der Waals parameters for hydrogen, the coordination sphere of a cation is found by setting the nonbonded distances in Eq. (38) to

$$r^{vdW} = A_r r - B_r \quad (39)$$

This moderate intervention gives quite good results for coordination geometries. Current work [33] is being done on coordination complexes of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ .

**2.1.3.8 Hydrogen bonds.** Starting from semi-empirical methods, different attempts have been made to find quantitative relations describing the gain in energy observed during formation of hydrogen bonds [34]. In some cases, electrostatic and van der Waals potentials alone give a good representation [35] of geometries and heats of formation for hydrogen bonded systems. This is true for PIMM.

If a heteroatom X with free electron pairs is present, we look for a hydrogen atom in a range of  $[(R_X + R_H)_{\text{covalent}} + 1.6 \text{ \AA}]$  away from it. The hydrogen must be bonded to another heteroatom Y to be able to keep up a polar attractive interaction with X. If such a hydrogen atom is present, the bond  $-\text{X}\cdots\text{H}-\text{Y}$  is defined and saved (HB) for the actual optimization cycle. The van der Waals interaction of the pair  $\text{X}\cdots\text{H}$ , repulsive at small distances, is cut off and the contribution of the hydrogen bond ( $E_{HB}$ ) to the overall energy is added through an increase in  $\sigma$ -polarisation for both H and X

$$q_H^{\sigma}(\text{HB}) = q_H^{\sigma} + 0.0125C_{HB}, \quad q_X^{\sigma}(\text{HB}) = q_X^{\sigma} - 0.0125C_{HB} \quad (40)$$

The scaling constant  $C_{HB}$  receives the value 1/2, if X and Y are part of a  $\pi$ -system; otherwise  $C_{HB}$  is set to unity. There is an additional gain in energy due to a reorganization of  $\pi$ -electrons while X and H approach. This makes the differentiation between saturated and unsaturated hydrogen bonded systems necessary.

#### 2.1.4 Energy calculation

The heat of formation of a molecular system  $H_f^{298}$ , is calculated from the bond energy  $E_B$ , the energy of deformation  $E_D$ , and the heats of formation of the free atoms,  $H_f^A$  (see Leroy [36])

$$H_f^{298} = E_B + E_D - \sum_A H_f^A \quad (41)$$

These terms will be specified in the following sections. The bond energy is expressed as a sum of  $\pi$  and  $\sigma$  contributions. The energy of deformation is the sum of the bond angle, van der Waals and electrostatic force-field terms. The heats of formation of the free atoms were taken from the literature [37].

**2.1.4.1  $\pi$ -Bond energy.** The diagonalization of the  $\pi$ -SCF Fock-matrix yields its eigenvalues and eigenvectors. From the latter, the density matrix  $P$  is built up (see Eq. (9)). The  $\pi$ -bond energy is then expressed as a function of the resonance and repulsion energies ( $\beta_{mn}$ ,  $G_{mm}$  and  $G_{nn}$ ), and of the ionization potentials of the atoms ( $I_m$ )

$$E^\pi = \sum_m \{1/2[1/2q_m^{\pi^2} - (q_m^\sigma - q_m^G) q_m^\pi] G_{mm} - I_m q_m^\pi - (Z_m - 1) G_{mm}\} + \sum_{m < n} [2\beta_{mn} - (1/2P_{mn}^2 - q_m^\pi q_n^\pi) G_{mn}] \quad (42)$$

The energy of the  $\sigma - \pi$  coupling appears in the first sum for electron densities on atom  $m$ . For covalently bonded atoms, the  $\sigma - \pi$  contribution is included in the  $\sigma$ -bond energy (Section 2.1.4.2); the nonbonding  $\sigma - \pi$  interactions are covered by the electrostatic potentials (Section 2.1.4.3).

**2.1.4.2  $\sigma$ -Bond energy.** The energy emerging from deviations of the interatomic distance from the equilibrium bond length  $r_{mn}^\circ$ , may be understood as the compressibility of the covalent bond and is characterized by a Morse potential

$$E^\sigma = - \sum_{m,n \text{ bonded}} D_{mn} [1. - (1. - \exp - \{a(r_{mn}^\circ - r_{mn})\})^2] \quad (43)$$

$D_{mn}$ , the dissociation energy of a polar  $\sigma$ -bond at the equilibrium length, is made a function of the  $\sigma$  and the  $\pi$  net charges on atoms  $m$  and  $n$

$$D_{mn} = D_{mn}^\circ + C_{mn} (q_m^\sigma q_n^\sigma + q_m^\sigma q_n^\pi + q_m^\pi q_n^\sigma) G_{mn}^\sigma \quad (44)$$

$G_{mn}^\sigma$  is the repulsion energy for  $\sigma$ -electrons (see  $\pi$ -SCF section).

**2.1.4.3 Energy of deformation.** The force field calculation delivers the strain energy as a criterion for the stability of the system. The terms contributing to the molecular heat of formation are gathered to give the energy of deformation  $E_D$ , which is the sum of angle deformations,  $E_\alpha$ ,  $E_\tau$ ,  $E_{\tau'}$ , van der Waals and electrostatic potentials,  $E_{vdW}$  and  $E_Q$

$$E_D = \sum_\alpha E_\alpha + \sum_\tau E_\tau + \sum_{\tau'} E_{\tau'} + \sum E_{vdW} + \sum E_Q \quad (45)$$

The first three sums run over the angles  $\alpha$ ,  $\tau$  and  $\tau'$ . The fourth sum runs over centres which are separated by more than three bonded atoms, and the last runs over all pairs  $m \cdots n$ .

The deformation of bonds was already included in the bond energy  $E_B = E^\sigma + E^\pi$  (Sections 2.1.4.1 and 2.1.4.2).

**2.1.4.4 Supplements.** Besides the trial geometry, the program needs some additional information. For example, the hybridization of atoms (e.g. C, N, O) must be specified. Before a calculation is run, the topological matrix is derived from the maximal covalent radii of the atoms (Sec-

tion 2.2; RBOND in the PIMM parameter list). The molecular topology remains constant during optimization, making it possible to compute and save energy contributions that are only dependent on the molecular topology.

After examining the molecular topology, some arrangements concerning the computation of the final bond energy are made.

- the bond to a tertiary (quaternary) carbon atom is made 0.0433 (0.0875) eV more stable, compared to a primary one;
- for polysubstituted bonds  $i - j$ , an electrostatic repulsion of  $0.025 (XI + XJ)^2$  eV for the lone pairs on heteroatomic substituents is added to the bond energy (XI and XJ are the number of heteroatoms bonded to  $i$  and  $j$ , respectively);
- for  $\pi$ -bonds with four substituents,  $-0.075$  eV are added.
- treatment of cyano groups: use of nitrogen parameters (label 3), an equilibrium angle of  $177^\circ$  at C, a bond length correction ( $-0.120$  Å), and an energy correction (4.22 eV).

The numeric values for the introduced corrections were chosen to give the experimental heats of formation of the corresponding substance classes within the computational error of the method.

### 2.1.5 Optimization procedure

The minimum of the strain energy  $E_S(q_1, q_2, q_3, \dots, q_N \equiv x_k)$  is to be found as a function of the  $3N$  coordinates  $q_i$  of the  $N$  atoms. The vector  $x_k$  characterizes the actual arrangement of the nuclei. Approximating  $E(x_k)$  by a quadratic function, convergence to the minimum is achieved in a single step, provided the partial derivatives of the energy function are known

$$(x_k - x) = -H^{-1}g_k \quad (46)$$

where  $H$  is the matrix of the second partial derivatives,

$$H_{ij} = d^2E/dq_i dq_j \quad \text{with } i, j = 1, 2, 3, \dots, 3N \quad (47)$$

and  $g_k$  is the vector of the first partial derivatives,

$$g_i = dE/dq_i \quad \text{with } i, j = 1, 2, 3, \dots, 3N \quad (48)$$

The magnitude of  $g_k$  corresponds to the sum of the internal forces of the system and its direction is that of steepest descent on the multidimensional potential surface.  $(x_k - x)$  is the required vector of the step lengths for the individual coordinate displacements. In praxis,  $H^{-1}$  is approximated by a matrix  $\alpha A$ , which is built up iteratively.

$$x_{k+1} = x_k - \alpha_k A_k g_k \quad (49)$$

The particular procedures working within this scheme differ in the determination of the matrix  $A$  and the scalar  $\alpha$ , which fixes the step length. In the present work, we follow the method of Murtagh and Sargent (MS) [38], setting  $\alpha = 1$  and  $A = 1$  (identity matrix) as initial values.  $A$  is then constructed by a recursion formula ( $T$  designs the transposed vector)

$$\begin{aligned}
A_k &= A_{k-1} + z_k z_k^T / c_k \\
\text{with } z_k &= A_{k-1} [g_k - (1 - \alpha_{k-1}) g_{k-1}] \\
\text{and } c_k &= (g_k - g_{k-1})^T z_k
\end{aligned} \tag{50}$$

After each step, the new energy value  $E_k$  is examined to make sure that  $E_k < E_{k-1}$ . Otherwise,  $\alpha_k$  is halved and the step is repeated.

As a criterion for convergence we choose an upper limit for the standard deviation of the components of the gradient vector  $g_k$ :

$$\left( \sum g_i^2 \right)^{1/2} / 3N \leq 0.5 \cdot 10^{-3} \text{ eV/\AA} \tag{51}$$

If the trial geometry is bad (far away from any minimum), instabilities may arise. To avoid these, the beginning step lengths are determined only by steepest descents. Then both  $\alpha$  and  $A$  are set to unity and kept constant

$$(x_k - x) = -1 g_k \tag{52}$$

Only when close enough to a minimum, at most after the first 10 cycles, the program switches to the described MS-procedure. Using standard bond lengths and angles as start geometry, generally 20 iteration steps are needed for convergence.

## 2.2 Parameters

In the present version, the program PIMM works with 10 atom types. These are read in together with the trial geometry and remain unchanged during the calculation. The labels are:

label	sort	label	sort	label	sort
0	>C< (sp3)	4	-O- (ether)	7	-Cl
1	>C= (sp2)	5	=O (acyl)	8	-F
2	>N- (pyrrole)	6	-S- (thioether)	9	-H
3	-N= (pyridine)				

The lists in Table 2 contain atomic constants and bonding or two-centre constants which are parameters attributed to one or two atoms, respectively. They are gathered in row vectors and square matrices with rows and columns standing for different atomic sorts. For vectors, the sequence of atomic constants is then

$$>C<, =C<, -N<, =N-, -O-, =O-, -S-, -Cl, -F, -H$$

and for the lower halve of matrices, the bonding constants are:

$$\begin{aligned}
&C(sp3) \cdot C(sp3); \\
&C(sp3) \cdot C(sp2), \quad C(sp2) \cdot C(sp2); \\
&C(sp3) \cdot N(sp3), \quad C(sp2) \cdot N(sp3), \quad N(sp3) \cdot N(sp3);
\end{aligned}$$

C(sp3)·N(sp2),	C(sp2)·N(sp2),	N(sp3)·N(sp2),	N(sp2)·N(sp2);				
C(sp3)·O(sp3),	C(sp2)·O(sp3),	N(sp3)·O(sp3),	N(sp2)·O(sp3),	*			
C(sp3)·O(sp2),	C(sp2)·O(sp2),	N(sp3)·O(sp2),	N(sp2)·O(sp2),	*	*		
C(sp3)·S(sp3),	C(sp2)·S(sp3),	*	*	*	*	*	
C(sp3)·Cl,	C(sp2)·Cl,	*	*	*	*	*	*
C(sp3)·F,	C(sp2)·F,	*	*	*	*	*	*
C(sp3)·H,	C(sp2)·H,	N(sp3)·H,	N(sp2)·H,	O(sp3)·H,	*	S(sp3)·H,	*

An asterisk is placed where the set of constants for the corresponding interaction is missing. This is the case for bonds, which do not or rarely occur in organic chemistry. For constants related only to the  $\pi$ -electronic system, the first and last element of vectors [C(sp<sup>3</sup>) and H], and the first column and last row of matrices [C(sp<sup>3</sup>)–X and X–H] are not defined.

In Table 1, we relate the constants appearing in the present text to the notation used in the FORTRAN-written program. Table 2 lists the parameters ordered as in the PIMM-BLOCK DATA. The constants for the  $\sigma$ -polarization are listed at the end of the section.

### 3 RESULTS

Some calculated and observed heats of formation are listed in Table 3. Most of the experimental data were taken from the compilations of Cox and Pilcher [37], and from Benson and co-workers [39]. Other references will be specified.

TABLE 1  
CONSTANTS USED IN THE PROGRAM PIMM

PIMM	Text	Reference (equation)
AL, BL	$a, b$	(26)
HA	$[\delta\alpha_m(\text{HMO})]$	Section 2.1.1
ZV	$N_m$	(10)
DHFA	$H_f^A$	(41)
HV	$I_m$	(7)
RV	$G_{mm}$	(7), (11)
ZS	$Z_{eff}(\text{Slater})$	(17)
RBOND	Maximal covalent radii	Section 2.1.4.4
QQ	$q_m^{\sigma^*}$	(7)
BK	$k_{mn}$	(14)
DE, DF	$D_{mn}^{\circ}, C_{mn}$	(44)
AME	$a$	(43)
GANG, DSW	$\alpha_i^{\circ}, 1/2 k_a(i)$	(29)
DECUB	$1/2 k'_a$	(30)
DBS	$1/2 k_i$	(34)
PK2, PK4, PK6	$a, b, c$	(28)
PPIZ	$1/2 k_{kl}$	(32)
PPIT, PTT	$k'_{kl}, k_{ij}$	(33)
A-, B-, C-, IVDW	$a, b, c, d$	(38)
XN, B, C	$a, b, c$	(19)
XP	$\chi_+$	(20)

TABLE 2  
PARAMETERS OF THE PROGRAM PIMM

BL (—)									
0.174;									
0.178,	0.177;								
0.178,	0.177,	0.177;							
0.185,	0.190,	0.190,	*;						
0.185,	0.190,	0.190,	*,	*;					
0.229,	*,	*,	*,	*,	*;				
0.230,	*,	*,	*,	*,	*,	*;			
0.230,	*,	*,	*,	*,	*,	*,	*		
AL (Å)									
1.533;									
1.508,	1.512;								
1.472,	1.442,	1.440;							
1.472,	1.460,	1.403,	1.440;						
1.426,	1.424,	1.405,	1.436,	*;					
1.426,	1.408,	1.404,	1.360,	*,	*;				
1.820,	1.787,	*,	*,	*,	*,	*;			
1.772,	1.755,	*,	*,	*,	*,	*,	*;		
1.380,	1.380,	*,	*,	*,	*,	*,	*;	*;	
1.100,	1.080,	1.030,	1.010,	1.000,	*,	1.335,	*,	*,	*;
HA (eV)									
0.000,	2.000,	1.000,	2.000,	1.000,	2.000,	2.000,	2.000;		
ZV (—)									
1.000,	2.000,	1.000,	2.000,	1.000,	2.000,	2.000,	2.000;		
DHFA (kJ/mol)									
715.3,	715.3,	473.0,	473.0,	249.3,	249.3,	274.8,	121.2,	78.95,	218.1;
HV (eV)									
11.16,	28.586,	14.12,	33.901,	17.697,	22.88,	25.32,	39.82;		
RV (eV)									
11.13,	16.628,	12.341,	18.60,	15.227,	11.90,	10.81,	21.025;		
ZS (—)									
3.18,	4.92,	3.55,	5.43,	4.18,	4.55,	4.50,	6.01;		
RBOND (Å)									
0.8,	0.8,	0.8,	0.8,	0.8,	0.8,	1.1,	1.2,	0.7,	0.4;
QQ (—)									
−0.0422,	−0.1224,	−0.300,	−0.040,	−0.360,	0.000,	−0.220,	−0.050,	−0.160,	0.0922;

(continued)

TABLE 2 (continued)

## BK (eV)

6.927;									
16.777,	17.876;								
6.635,	10.845,	6.820;							
14.000,	23.698,	14.371,	*;						
9.622,	16.250,	8.720,	*,	*;					
20.000,	*,	*,	*,	*,	*;				
18.500,	*,	*,	*,	*,	*,	*;			
15.000,	*,	*,	*,	*,	*,	*,	*;	*;	

## DF (—)

0.300;									
0.300,	0.200;								
0.200,	0.000,	0.250;							
0.000,	0.000,	0.250,	0.200;						
0.000,	0.000,	0.250,	0.250,	*;					
0.000,	0.500,	0.250,	0.250,	*,	*;				
0.000,	0.000,	*,	*,	*,	*,	*;			
0.000,	1.000,	*,	*,	*,	*,	*,	*;		
0.000,	1.000,	*,	*,	*,	*,	*,	*,	*;	
—0.640,	—0.640,	0.640,	0.640,	0.400	*,	0.700,	*,	*,	*;

## DE (eV)

3.5640;									
3.9922,	4.1368;								
3.0000,	2.9048,	1.9168;							
3.5522,	3.5412,	3.1660,	3.1900;						
3.4008,	3.9786,	2.4720,	3.2486,	*;					
3.5780,	4.0482,	4.8320,	3.4624,	*,	*;				
2.9724,	3.4012,	*,	*,	*,	*,	*;			
3.5254,	3.8686,	*,	*,	*,	*,	*,	*;		
4.7514,	5.2464,	*,	*,	*,	*,	*,	*,	*;	
4.2475,	4.3172,	3.7900,	4.0208,	3.8987,	*,	3.6102,	*,	*,	*;

## GANG (rad)

1.9199,	2.0944,	2.0071,	2.0944,	1.9548,	2.0944,	1.8326,	*,	*,	*;
---------	---------	---------	---------	---------	---------	---------	----	----	----

AME ( $\text{\AA}^{-1}$ )

1.8407;									
1.8641,	2.0022;								
1.2959,	1.9209,	2.5290;							
1.2959,	1.9209,	2.5290,	2.5290;						
1.0838,	1.7870,	2.0275,	2.0275,	*;					
1.0838,	1.7870,	2.0275,	2.0275,	*,	*;				
1.9663,	1.9663,	*,	*,	*,	*,	*;			
1.8000,	1.8000,	*,	*,	*,	*,	*,	*;		
1.8000,	1.8000,	*,	*,	*,	*,	*,	*,	*;	
1.3800,	1.3320,	1.4690,	1.4690,	1.2400,	*,	1.500,	*,	*,	*;

DSW ( $\text{mdyn} \cdot \text{\AA} \cdot \text{rad}^{-2} \cdot 10^{-3}$ )

0.572,	0.442,	0.486,	0.798,	0.668,	0.752,	0.800,	*,	*,	*;
--------	--------	--------	--------	--------	--------	--------	----	----	----

(continued)

TABLE 2 (continued)

DECUB (mdyn·Å·rad <sup>-1</sup> ·10 <sup>-3</sup> )									
-1.246,	-0.662,	*	*	*	*	*	*	*	*
DBS (mdyn·Å·rad <sup>-2</sup> ·10 <sup>-3</sup> )									
0.000,	0.411,	*	*	*	*	*	*	*	*
PK2 (mdyn·Å)									
-31.514;									
-31.515,	-31.514;								
-22.292,	-22.292,	-56.632;							
-22.292,	-22.292,	-56.632,	-56.632;						
-20.067,	-20.067,	18.267,	18.267,	*					
-20.067,	-20.067,	18.267,	18.267,	*	*				
-66.726,	-66.726,	*	*	*	*	*			
10.770,	10.770,	*	*	*	*	*	*		
11.380,	11.380,	*	*	*	*	*	*	*	
PK4 (mdyn·Å <sup>3</sup> )									
130.072;									
130.072,	130.072;								
67.003,	67.003,	179.565;							
67.003,	67.003,	179.565,	179.565;						
52.681,	52.681,	-61.330,	-61.330,	*					
52.681,	52.681,	-61.330,	-61.330,	*	*				
261.520,	261.520,	*	*	*	*	*			
0.000,	0.000,	*	*	*	*	*	*		
0.000,	0.000,	*	*	*	*	*	*	*	
PK6 (mdyn·Å <sup>5</sup> )									
-70.269;									
-70.269,	-70.269;								
-6.018,	-6.018,	-94.043;							
-6.018,	-6.018,	-94.043,	-94.043;						
3.629,	3.629,	75.710,	75.710,	*					
3.629,	3.629,	75.710,	75.710,	*	*				
0.000,	0.000,	*	*	*	*	*			
0.000,	0.000,	*	*	*	*	*	*		
0.000,	0.000,	*	*	*	*	*	*	*	
PPIZ (mdyn·Å·10 <sup>-5</sup> )									
1.67;									
1.2,	1.2;								
1.0,	1.0,	0.8;							
1.0,	1.0,	0.8,	0.8;						
0.9,	0.9,	0.8,	0.8,	0.8;					
0.9,	0.9,	0.8,	0.8,	0.8,	0.8;				
1.2,	1.2,	1.2,	1.2,	1.2,	1.2,	1.2;			
1.2,	1.2,	1.2,	1.2,	1.2,	1.2,	1.2,	1.2;		
1.2,	1.2,	1.2,	1.2,	1.2,	1.2,	1.2,	1.2,	1.2;	
0.78,	1.0,	1.0,	1.0,	0.9,	0.9,	1.0,	1.0,	1.0,	0.58;

(continued)



TABLE 2 (continued)

PPIT (mdyn·Å·10<sup>-5</sup>)

1.67;									
1.67,	1.67;								
1.0,	1.0,	0.8;							
1.0,	1.0,	0.8,	0.8;						
0.9,	0.9,	0.8,	0.8,	0.8;					
0.9,	0.9,	0.8,	0.8,	0.8,	0.8;				
1.2,	1.2,	1.2,	1.2,	1.2,	1.2,	1.2;			
1.2,	1.2,	1.2,	1.2,	1.2,	1.2,	1.2,	1.2;		
1.2,	1.2,	1.2,	1.2,	1.2,	1.2,	1.2,	1.2,	1.2;	
1.1,	1.1,	1.0,	1.0,	0.9,	0.9,	1.0,	1.0,	1.0,	0.58;

PTT (—)

0.14;									
0.04,	0.00;								
0.04,	0.00,	0.00;							
0.02,	0.00,	0.00,	*;						
0.00,	0.00,	0.00,	*,	*;					
0.00,	*,	*,	*,	*,	*;				
0.00,	*,	*,	*,	*,	*,	*;			
0.00,	*,	*,	*,	*,	*,	*,	*;		

AVDW (kJ·mol<sup>-1</sup>·Å<sup>1vdw</sup>·10<sup>6</sup>)

1.261;									
1.261,	1.261;								
1.423,	1.423,	1.620;							
1.423,	1.423,	1.620,	1.620;						
1.167,	1.167,	1.324,	1.324,	1.084;					
1.167,	1.167,	1.324,	1.324,	1.084,	1.084;				
1.069,	1.069,	1.206,	1.206,	1.001,	1.001,	0.924;			
1.069,	1.069,	1.206,	1.206,	1.001,	1.001,	0.924,	0.924;		
0.472,	0.472,	0.512,	0.512,	0.406,	0.406,	0.362,	0.362,	0.227;	
0.404,	0.188,	0.218,	0.218,	0.176,	0.176,	0.1695,	0.1695,	0.0523,	0.0276;

BVDW (Å<sup>-1</sup>)

0.000;									
0.000,	0.000;								
0.000,	0.000,	0.000;							
0.000,	0.000,	0.000,	0.000;						
0.000,	0.000,	0.000,	0.000,	0.000;					
0.000,	0.000,	0.000,	0.000,	0.000,	0.000;				
1.811,	1.811,	1.811,	1.811,	1.811,	1.811,	3.621;			
1.811,	1.811,	1.811,	1.811,	1.811,	1.811,	3.621,	3.621;		
1.940,	1.940,	1.940,	1.940,	1.940,	1.940,	3.621,	3.621,	3.621;	
1.795,	2.040,	2.040,	2.040,	2.040,	2.040,	3.851,	3.851,	4.080,	4.896;

(continued)

TABLE 2 (*continued*)

CVDW (kJ·mol <sup>-1</sup> ·Å <sup>6</sup> ·10 <sup>3</sup> )									
1.370;									
1.370,	1.370;								
1.423,	1.423,	1.482;							
1.423,	1.423,	1.482,	1.482;						
1.433,	1.433,	1.490,	1.490,	1.499;					
1.433,	1.433,	1.490,	1.490,	1.499,	1.499;				
2.863,	2.863,	2.978,	2.978,	2.995,	2.995,	5.986;			
2.863,	2.863,	2.978,	2.978,	2.995,	2.995,	5.986,	5.986;		
0.645,	0.645,	0.645,	0.645,	2.079,	2.079,	2.652,	2.652,	0.566;	
1.126,	0.523,	0.553,	0.553,	0.5555,	0.5555,	1.110,	1.110,	0.497,	0.0691;
IVDW (—)									
12;									
12,	12;								
12,	12,	12;							
12,	12,	12,	12;						
12,	12,	12,	12,	12;					
12,	12,	12,	12,	12,	12;				
6,	6,	6,	6,	6,	6,	0;			
6,	6,	6,	6,	6,	6,	0,	0;		
6,	6,	6,	6,	6,	6,	0,	0,	0;	
6,	6,	6,	6,	6,	6,	0,	0,	0,	0;
Parameters for the $\sigma$ -formalism									
XN (eV)									
7.98,	8.79,	11.54,	12.87,	14.18,	17.07,	10.14,	11.00,	14.66,	7.17;
B (eV)									
9.18,	9.32,	10.82,	11.15,	12.92,	13.79,	9.13,	9.69,	13.85,	6.24;
C (eV)									
1.88,	0.51,	1.36,	0.85,	1.39,	0.47,	1.38,	1.35,	2.31,	—0.56;
XP (eV)									
19.04,	19.62,	23.72,	24.87,	28.94,	31.33,	20.65,	22.04,	30.82,	15.00;

We performed calculations on the bimolecular systems Mohammad and Hopfinger [34] used to parametrize their treatment of hydrogen bonds at the MINDO and CNDO levels. The equilibrium geometries and dissociation energies delivered by PIMM are in good agreement with experiment (Table 4). Additionally, an association of 22 water molecules and a cluster of 5 chloroform molecules have been studied in order to estimate their heats of sublimation. For the 22 water molecules with tetrahedral environments for the oxygen atoms, we obtain a 49.6 kJ/mol heat of sublimation compared to 47 kJ/mol from the experimental heats of fusion and vaporization [40]. The polar H...Cl interaction is weaker than H...O or H...N, but by no means negligible.

The conformations (1)–(3) for acids and esters, and (3)–(5) for amides (Scheme 1) were exam-

TABLE 3  
CALCULATED AND OBSERVED HEATS OF FORMATION

Molecule	PIMM	Experiment
<i>n</i> -Butane, <i>antiperiplanar</i>	−127	−128 <sup>c</sup>
<i>n</i> -Butane, <i>synclinal</i>	−123	−124 <sup>a</sup>
<i>n</i> -Butane, <i>anticlinal</i>	−113	−113 <sup>d</sup>
<i>n</i> -Butane, <i>synperiplanar</i>	−101	−102 <sup>d</sup>
<i>cis</i> -1,2-Dimethylcyclopentane	−114	−130 <sup>b</sup>
<i>trans</i> -1,2-Dimethylcyclopentane	−120	−137 <sup>b</sup>
<i>cis</i> -1,3-Dimethylcyclopentane	−117	−136 <sup>b</sup>
<i>trans</i> -1,3-Dimethylcyclopentane	−125	−134 <sup>b</sup>
Methylcyclohexane	−152	−155 <sup>a</sup>
1,1-Dimethylcyclohexane	−179	−181 <sup>a</sup>
<i>trans</i> -1,2-Dimethylcyclohexane	−178	−180 <sup>b</sup>
<i>cis</i> -1,2-Dimethylcyclohexane	−169	−172 <sup>b</sup>
<i>cis</i> -Bicyclo[3.3.0]octane	−65	−93 <sup>e</sup>
<i>trans</i> -Bicyclo[3.3.0]octane	−47	−67 <sup>e</sup>
<i>trans</i> -Decalin	−180	−182 <sup>a</sup>
<i>cis</i> -Decalin	−167	−169 <sup>a</sup>
Dicyclopropyl	131	129 <sup>a</sup>
Butadiene, <i>trans</i>	109	109 <sup>a</sup>
Butadiene, <i>cis</i>	111	118 <sup>a</sup>
Benzene	78	83 <sup>a</sup>
Fulvene	209	199 <sup>a</sup>
Cyclooctatetraene, <i>tube</i>	305	298 <sup>a</sup>
1,2-Dihydronaphthalene	119	127 <sup>b</sup>
1,4-Dihydronaphthalene	135	139 <sup>b</sup>
Norbornadiene	236	250 <sup>a</sup>
Cycloheptatriene	183	184 <sup>a</sup> /187 <sup>b</sup>
Toluene	45	50 <sup>a</sup>
<i>o</i> -Xylene	18	19 <sup>b</sup>
<i>m</i> -Xylene	12	17 <sup>b</sup>
<i>p</i> -Xylene	13	18 <sup>b</sup>
Benzyl alcohol	−89	−94 <sup>b</sup>
Vinyl alcohol	−132	−124 <sup>b</sup>
Phenol	−108	−97 <sup>b</sup>
<i>o</i> -Cresol	−137	−129 <sup>b</sup>
<i>m</i> -Cresol	−143	−132 <sup>b</sup>
<i>p</i> -Cresol	−134	−126 <sup>b</sup>
Anisole	−81	−75 <sup>b</sup>
Divinyl ether	−23	−13 <sup>b</sup>
Diphenyl ether	26	−42 <sup>b</sup>
Furan	−3	−35 <sup>b</sup>
Formaldehyde	−110	−108 <sup>f</sup>
<i>p</i> -Benzoquinone	−168	−144 <sup>f</sup>
Acetaldehyde	−163	−166 <sup>b</sup>
Acetone	−226	−216 <sup>b</sup>
Cyclopentanone	−204	−190 <sup>b</sup>
Cyclohexanone	−239	−222 <sup>b</sup>
2,3-Butanedione (Biacetyl)	−431	−329 <sup>b</sup>
2,4-Pentanedione (Acetylacetone)	−401	−378 <sup>b</sup>

(continued)

TABLE 3 (*continued*)

Molecule	PIMM	Experiment
Acetic acid	−474	−432 <sup>f</sup> /−435 <sup>b</sup>
Oxalic acid	−996	−733 <sup>f</sup>
Methyl formate	−328	−339 <sup>b</sup> /−350 <sup>f</sup>
Methyl benzoate	−311	−300 <sup>b</sup>
Acetic anhydride	−658	−577 <sup>b</sup>
Maleic anhydride	−468	−410 <sup>b</sup> /−399 <sup>f</sup>
Tetrahydrothiophene	−8	−34 <sup>b</sup>
Tetrahydrothiopyran	−52	−63 <sup>b</sup>
Benzyl mercaptan	97	92 <sup>b</sup>
Thiophene	117	116 <sup>b</sup>
Thiophenol	87	112 <sup>b</sup>
Thioanisole	75	98 <sup>b</sup>
Diphenyl sulfide	192	231 <sup>b</sup>
Methylamine	−21	−23 <sup>b</sup>
Dimethylamine	−33	−19 <sup>b</sup>
Trimethylamine	−26	−25 <sup>b</sup>
Aniline	83	87 <sup>b</sup>
<i>N</i> -Methylaniline	83	90 <sup>b</sup>
<i>N,N</i> -Dimethylaniline	104	95 <sup>b</sup> /101 <sup>g</sup>
Diphenylamine	229	209 <sup>b</sup>
Pyrrole	81	103 <sup>b</sup> /108 <sup>b</sup>
Indole	172	187 <sup>g</sup>
Pyridine	141	140 <sup>b</sup> /145 <sup>f</sup>
Pyridazine	282	278 <sup>b</sup>
Pyrimidine	172	197 <sup>b</sup>
Pyrazine	182	196 <sup>b</sup>
Indazole	262	249 <sup>g</sup>
Benzotriazole	403	337 <sup>g</sup>
Oxazole	1	−15 <sup>i</sup>
Isoxazole	154	79 <sup>h</sup>
Nitromethane	−75	−75 <sup>b</sup>
Acetonitrile	94	80 <sup>b</sup> /88 <sup>f</sup>
Benzonitrile	224	215 <sup>f</sup> /219 <sup>b</sup>
Chloromethane	−86	−82 <sup>f</sup>
Dichloromethane	−106	−96 <sup>a</sup>
Trichloromethane	−108	−102 <sup>a</sup>
Tetrachloromethane	−113	−103 <sup>f</sup>
Chlorobenzene	43	52 <sup>b</sup>
<i>o</i> -Dichlorobenzene	25	30 <sup>b</sup>
<i>m</i> -Dichlorobenzene	10	25 <sup>b</sup>
<i>p</i> -Dichlorobenzene	3	22 <sup>f</sup>
Fluoromethane	−257	−280 <sup>f</sup>
Difluoromethane	−449	−449 <sup>f</sup>
Trifluoromethane	−654	−691 <sup>f</sup>
Tetrafluoromethane	−957	−931 <sup>f</sup>
2,2'-Difluorobiphenyl	−194	−195 <sup>b</sup>
4,4'-Difluorobiphenyl	−208	−200 <sup>b</sup>
<i>p</i> -Fluorotoluene	−139	−145 <sup>b</sup>

<sup>a</sup> From Ref. [37]; <sup>b</sup> From Ref. [39]; <sup>c</sup> From Ref. [46]; <sup>d</sup> From Ref. [47]; <sup>e</sup> From Ref. [48]; <sup>f</sup> From Ref. [49]; <sup>g</sup> From Ref. [50];

<sup>h</sup> From Ref. [51]; <sup>i</sup> From Ref. [52]. Calculated and experimental  $H_f^{gas}$  values in kJ/mol.

TABLE 4  
GEOMETRIES AND ENERGETICS OF HYDROGEN BONDS IN THE GAS PHASE

System	A-H...B	$R_{AB}$ [Å] PIMM (experiment <sup>a</sup> )	$H_f$ /H-bond [kJ/mol] PIMM (experiment <sup>a</sup> )
(HCOOH) <sub>2</sub>	-O-H...O=	2.70 (2.70)	23.4 (29.3)
(CH <sub>3</sub> COOH) <sub>2</sub>	-O-H...O=	2.66 (2.68 <sup>b</sup> )	29.3 (31.4)
(CCl <sub>3</sub> COOH) <sub>2</sub>	-O-H...O=	2.72 (2.76)	26.4
(CH <sub>3</sub> OH) <sub>2</sub>	-O-H...O-	2.86	23.8 (25.1)
(HCONH <sub>2</sub> ) <sub>2</sub>	>N-H...O=	2.81 (2.90)	28.0 (29.3)
CH <sub>3</sub> CN-CH <sub>3</sub> OH	-O-H...N≡	2.94	18.8 (16.7)
Pyridine-CH <sub>3</sub> OH	-O-H...N=	2.91	20.1 (16.7)
(H <sub>2</sub> O) <sub>22</sub>			24.8
(CHCl <sub>3</sub> ) <sub>5</sub>			1.9

<sup>a</sup> Experimental values as listed in Ref. [34].

<sup>b</sup> From Ref. [53].

ined. The computed energy differences for *cis-trans* isomers and the potential barriers between them are listed in Table 5; '*perp*' designs the conformation (3) with the X-R' bond perpendicular to the R-C=O plane.

Table 6 collects structural features calculated by PIMM and the corresponding experimental data for several organic molecules. The calculated dipole moments are compared with experimental values for some characteristic molecules in Table 7.

#### 4 DISCUSSION

The experimental heats of formation, derived in most cases from heats of combustion, are re-

Scheme 1. Conformations of acids and esters.

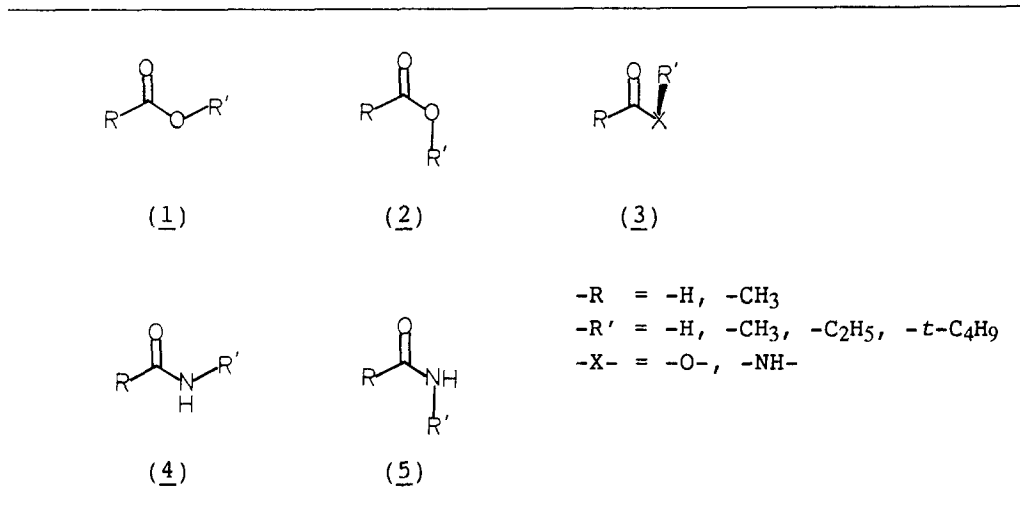
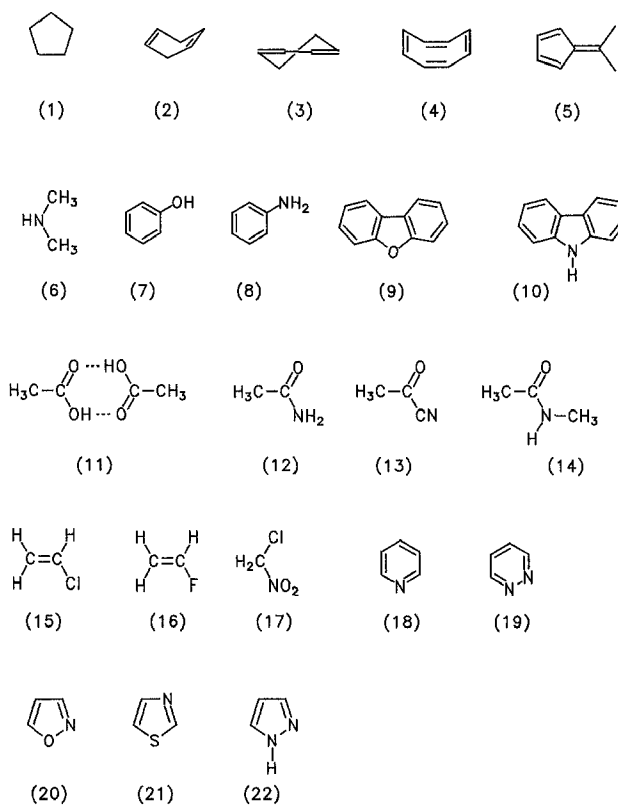


TABLE 5  
ENERGY DIFFERENCES AND ROTATIONAL BARRIERS FOR *CIS-TRANS* ISOMERS

Molecule	Structure	PIMM (experiment) <sup>a</sup>		
		$\Delta\Delta H_f^{cis-trans}$	$\Delta\Delta H_f^{trans-perp}$	$\Delta\Delta H_f^{cis-perp}$
Formic acid	HCOOH	17 (20 <sup>b</sup> )	50 (52 <sup>b</sup> )	32 (32 <sup>b</sup> )
Acetic acid	H <sub>3</sub> CCOOH	19 (30 <sup>b</sup> )	50 (55 <sup>b</sup> )	31 (25 <sup>b</sup> )
Methyl formate	HCOOCH <sub>3</sub>	15 (15 <sup>b</sup> )	41 (47 <sup>b</sup> )	26 (32 <sup>b</sup> )
Ethyl formate	HCOOCH <sub>2</sub> CH <sub>3</sub>	14 (8–13 <sup>c</sup> )	38 (33 <sup>d</sup> )	24 (25 <sup>d</sup> )
<i>t</i> -Butyl formate	HCOOC(CH <sub>3</sub> ) <sub>3</sub>	14 (1 <sup>e</sup> , 5 <sup>f</sup> , 9 <sup>g</sup> )	32 (43 <sup>f</sup> )	18 (38 <sup>f</sup> )
Formamide	HCONH <sub>2</sub>	–	106 (84 <sup>h</sup> , 95 <sup>i</sup> )	106 (84 <sup>h</sup> , 95 <sup>i</sup> )
<i>N</i> -Methylformamide	HCONHCH <sub>3</sub>	10 (7 <sup>i</sup> )	100 (86 <sup>j</sup> )	90 (79 <sup>j</sup> )
<i>N</i> -Methylacetamide	H <sub>3</sub> CCONHCH <sub>3</sub>	6 (12 <sup>k</sup> , 15 <sup>i</sup> )	88 (95 <sup>k</sup> )	82 (83 <sup>k</sup> )

<sup>a</sup> All values in kJ/mol; <sup>b</sup> Ref. [54]; <sup>c</sup> Ref. [55]; <sup>d</sup> Ref. [56]; <sup>e</sup> Ref. [57]; <sup>f</sup> Ref. [58]; <sup>g</sup> Ref. [59]; <sup>h</sup> Ref. [60]; <sup>i</sup> Ref. [61]; <sup>j</sup> Ref. [62]; <sup>k</sup> Ref. [63].

TABLE 6  
CALCULATED AND OBSERVED MOLECULAR GEOMETRIES



(continued)

TABLE 6 (continued))

1	C <sup>1</sup> –C <sup>2</sup> 1.535 (1.546), C <sup>2</sup> –C <sup>3</sup> 1.530 (1.546), C <sup>1</sup> –C <sup>5</sup> 1.535 (1.546), C–H 1.099 (1.113); C <sup>1</sup> –C <sup>2</sup> –C <sup>3</sup> 103.7 (103.9), C <sup>2</sup> –C <sup>3</sup> –C <sup>4</sup> 101.6 (102.1), C <sup>5</sup> –C <sup>1</sup> –C <sup>2</sup> 105.8 (106.1); C <sup>2</sup> –C <sup>1</sup> –C <sup>5</sup> –C <sup>4</sup> 0.5 (0), C <sup>1</sup> –C <sup>2</sup> –C <sup>3</sup> –C <sup>4</sup> 42 (40), C <sup>5</sup> –C <sup>1</sup> –C <sup>2</sup> –C <sup>3</sup> 26 (25). /ED [64], (C <sub>3</sub> –Symmetry)
2	C <sup>1</sup> = C <sup>2</sup> 1.346 (1.350), C <sup>2</sup> –C <sup>3</sup> 1.468 (1.468), C <sup>1</sup> –C <sup>6</sup> 1.508 (1.523), C <sup>5</sup> –C <sup>6</sup> 1.530 (1.534); C <sup>1</sup> –C <sup>2</sup> –C <sup>3</sup> 120.7 (120.1), C <sup>6</sup> –C <sup>1</sup> –C <sup>2</sup> 119.5 (–), C <sup>1</sup> –C <sup>6</sup> –C <sup>5</sup> 111.3 (–); C <sup>1</sup> –C <sup>2</sup> –C <sup>3</sup> –C <sup>4</sup> 13 (18), C <sup>2</sup> –C <sup>1</sup> –C <sup>6</sup> –C <sup>5</sup> 34 (–), C <sup>4</sup> –C <sup>5</sup> –C <sup>6</sup> –C <sup>1</sup> 47 (–). /ED [65]
3	C = C 1.339 (1.347), C–C 1.508 (1.511); C = C–C 121.4 (122.7), C–C–C 113.9 (111.9); $\Phi^{fold}$ :159.8 (159.3). /ED [65]
4	C = C 1.342 (1.340, 1.330), C–C 1.489 (1.476, 1.456); C = C–C 125.4 (126.1, 126.8), C = C–C = C 59.6 (43.1, 55.7). (ED [66], /XR [67])
5	C <sup>1</sup> –C <sup>2</sup> 1.468 (1.476), C <sup>2</sup> –C <sup>3</sup> 1.355 (1.340), C <sup>3</sup> –C <sup>4</sup> 1.454 (1.462), C <sup>1</sup> –C <sup>6</sup> 1.356 (1.347), C <sup>6</sup> –C <sup>7</sup> 1.509 (1.510); C <sup>2</sup> –C <sup>1</sup> –C <sup>5</sup> 105.5 (–), C <sup>1</sup> –C <sup>2</sup> –C <sup>3</sup> 108.2 (–), C <sup>2</sup> –C <sup>3</sup> –C <sup>4</sup> 109.0 (109.0), C <sup>2</sup> –C <sup>1</sup> –C <sup>6</sup> 127.2 (–), C <sup>1</sup> –C <sup>6</sup> –C <sup>7</sup> 121.1 (122.0), C <sup>7</sup> –C <sup>6</sup> –C <sup>8</sup> 117.8 (–); C <sup>2</sup> –C <sup>1</sup> –C <sup>6</sup> –C <sup>7</sup> 1 (–), C <sup>2</sup> –C <sup>1</sup> –C <sup>6</sup> –C <sup>8</sup> 179 (–). /ED [68]
6	C–N 1.471 (1.455), C–H 1.099 (1.106), N–H 1.014 (1.00); C–N–C 114.2 (111.8). /ED [69]
7	C–O 1.388 (1.375), C <sup>1</sup> –C <sup>2</sup> 1.397 (1.391), C <sup>2</sup> –C <sup>3</sup> 1.396 (1.392), C <sup>3</sup> –C <sup>4</sup> 1.397 (1.395), C <sup>4</sup> –C <sup>5</sup> 1.396 (1.394), C <sup>1</sup> –C <sup>6</sup> 1.397 (1.391); C <sup>2</sup> –C <sup>1</sup> –C <sup>6</sup> 120.1 (120.9), C <sup>1</sup> –C <sup>2</sup> –C <sup>3</sup> 120.0 (119.2), C <sup>2</sup> –C <sup>3</sup> –C <sup>4</sup> 120.0 (120.8), C <sup>3</sup> –C <sup>4</sup> –C <sup>5</sup> 119.9 (119.2), C <sup>4</sup> –C <sup>5</sup> –C <sup>6</sup> 120.2 (120.5), C <sup>1</sup> –C <sup>6</sup> –C <sup>5</sup> 119.8 (119.4), C <sup>2</sup> –C <sup>1</sup> –O 119.8 (117.0), C <sup>6</sup> –C <sup>1</sup> –O 120.1 (122.1), C <sup>1</sup> –O–H 112.6 (108.8). /MW [70]
8	C <sup>1</sup> –C <sup>2</sup> 1.402 (1.397), C <sup>2</sup> –C <sup>3</sup> 1.395 (1.394), C <sup>3</sup> –C <sup>4</sup> 1.397 (1.396), C–N 1.385 (1.402); C <sup>6</sup> –C <sup>1</sup> –C <sup>2</sup> 120.2 (119.4), C <sup>1</sup> –C <sup>2</sup> –C <sup>3</sup> 119.7 (120.1), C <sup>2</sup> –C <sup>3</sup> –C <sup>4</sup> 120.3 (120.7), C <sup>3</sup> –C <sup>4</sup> –C <sup>5</sup> 119.9 (118.9). /MW [71]
9	O–C <sup>1</sup> 1.393 (1.418), C <sup>1</sup> –C <sup>2</sup> 1.393 (1.401), C <sup>2</sup> –C <sup>3</sup> 1.399 (1.383), C <sup>3</sup> –C <sup>4</sup> 1.401 (1.377), C <sup>4</sup> –C <sup>5</sup> 1.398 (1.386), C <sup>5</sup> –C <sup>6</sup> 1.396 (1.387), C <sup>1</sup> –C <sup>6</sup> 1.412 (1.382), C <sup>6</sup> –C <sup>6'</sup> 1.473 (1.480), C–O–C 105.3 (104.4), O–C <sup>1</sup> –C <sup>6</sup> 112.1 (112.9), C <sup>1</sup> –C <sup>6</sup> –C <sup>6'</sup> 105.2 (105.6), O–C <sup>1</sup> –C <sup>2</sup> 128.1 (123.2), C <sup>2</sup> –C <sup>1</sup> –C <sup>6</sup> 119.8 (123.9), C <sup>1</sup> –C <sup>2</sup> –C <sup>3</sup> 118.1 (115.3), C <sup>2</sup> –C <sup>3</sup> –C <sup>4</sup> 121.6 (122.1), C <sup>3</sup> –C <sup>4</sup> –C <sup>5</sup> 120.9 (121.4), C <sup>4</sup> –C <sup>5</sup> –C <sup>6</sup> 117.2 (118.5), C <sup>1</sup> –C <sup>6</sup> –C <sup>5</sup> 122.4 (118.9). /XR [72]
10	N–C <sup>1</sup> 1.384 (1.414), N–H 1.020 (0.964), C <sup>1</sup> –C <sup>2</sup> 1.407 (1.395), C <sup>2</sup> –C <sup>3</sup> 1.391 (1.390), C <sup>3</sup> –C <sup>4</sup> 1.410 (1.398), C <sup>4</sup> –C <sup>5</sup> 1.390 (1.395), C <sup>5</sup> –C <sup>6</sup> 1.404 (1.400), C <sup>1</sup> –C <sup>6</sup> 1.412 (1.404), C <sup>6</sup> –C <sup>6'</sup> 1.466 (1.467), C–N–C 109.1 (108.3), N–C <sup>1</sup> –C <sup>6</sup> 109.2 (108.8), C <sup>1</sup> –C <sup>6</sup> –C <sup>6'</sup> 106.2 (107.1), N–C <sup>1</sup> –C <sup>2</sup> 130.5 (128.9), C <sup>2</sup> –C <sup>1</sup> –C <sup>6</sup> 120.3 (122.3), C <sup>1</sup> –C <sup>2</sup> –C <sup>3</sup> 117.6 (117.7), C <sup>2</sup> –C <sup>3</sup> –C <sup>4</sup> 121.8 (121.3), C <sup>3</sup> –C <sup>4</sup> –C <sup>5</sup> 121.1 (120.4), C <sup>4</sup> –C <sup>5</sup> –C <sup>6</sup> 117.3 (119.5), C <sup>1</sup> –C <sup>6</sup> –C <sup>5</sup> 121.8 (118.8). /XR [73]
11	C = O 1.209 (1.231), C–O 1.359 (1.334), C–C 1.508 (1.506); C–C = O 119.0 (123.6), C–C–O 119.9 (113.0), O...O 2.661 (2.680). /ED [53]
12	C = O 1.215 (1.220, 1.247), C–C 1.508 (1.519, 1.508), C–N 1.372 (1.380, 1.330), N–H 1.021 (1.022); C–C–N 120.8 (115.1, 116.8), N–C–O 120.0 (122.0, 122.4). /ED [74], /XR [75]
13	C <sup>1</sup> –C <sup>2</sup> 1.508 (1.518), C <sup>2</sup> = O 1.210 (1.208), C <sup>2</sup> –C <sup>3</sup> 1.492 (1.477), C <sup>3</sup> = N 1.159 (1.167); C <sup>1</sup> –C <sup>2</sup> –C <sup>3</sup> 120.8 (114.2), C <sup>1</sup> –C <sup>2</sup> –O 119.8 (124.6), C <sup>2</sup> –C <sup>3</sup> = N 178.1 (179.2). /ED and MW [76]
14	C <sup>2</sup> = O 1.216 (1.225), C <sup>1</sup> –C <sup>2</sup> 1.507 (1.520), C <sup>2</sup> –N 1.376 (1.386), N–C <sup>4</sup> 1.477 (1.469); C <sup>1</sup> –C <sup>2</sup> –N 119.0 (114.1), O = C <sup>2</sup> –N 123.8 (121.8), C <sup>2</sup> –N–C <sup>4</sup> 122.2 (–). /ED [77]
15	C = C 1.341 (1.355), C–Cl 1.720 (1.728); C = C–Cl 120.0 (121.1). /ED [78]
16	C = C 1.340 (1.332), C–F 1.344 (1.348). /MW [79]
17	C–Cl 1.767 (1.765), C–N 1.482 (1.493), N–O 1.245 (1.230); Cl–C–N 111.5 (114), O–N–O 124.5 (128). /ED [80]
18	C–N 1.338 (1.338), C <sup>1</sup> –C <sup>2</sup> 1.397 (1.394), C <sup>2</sup> –C <sup>3</sup> 1.395 (1.392), C <sup>1</sup> –H 1.079 (1.086), C <sup>2</sup> –H 1.078 (1.082), C <sup>3</sup> –H 1.079 (1.081); C–N–C 120.7 (116.9), N–C–C 121.2 (123.8), C–C <sup>2</sup> –C 119.1 (118.5), C–C <sup>3</sup> –C 118.7 (118.4). /MW [81]
19	N–N 1.346 (1.330), C–N 1.323 (1.335), C <sup>1</sup> –C <sup>2</sup> 1.412 (1.381), C <sup>2</sup> –C <sup>2'</sup> 1.380 (1.375), C–N–N 121.2 (119.0), N–C–C 120.5 (123.7), C–C–C 118.3 (117.3). /MW [82]
20	O–C 1.386 (1.344), O–N 1.424 (1.399), C = C 1.348 (1.356), C–C 1.452 (1.425), C = N 1.288 (1.309); C–O–N 104.0 (108.8), C = C–O 110.6 (110.6), C–C = C 106.4 (103.0), C–C = N 107.3 (112.3), C = N–O 111.7 (105.3). /MW [83]
21	S–C <sup>2</sup> 1.707 (1.724), S–C <sup>5</sup> 1.714 (1.713), C <sup>2</sup> = N 1.301 (1.304), N–C <sup>4</sup> 1.390 (1.372), C <sup>4</sup> –C <sup>5</sup> 1.359 (1.367); C <sup>5</sup> –S–C <sup>2</sup> 93.0 (89.3), S–C <sup>2</sup> –N 110.2 (115.2), C <sup>2</sup> –N–C <sup>4</sup> 114.8 (110.1), N–C <sup>4</sup> –C <sup>5</sup> 113.6 (115.8), C <sup>4</sup> –C <sup>5</sup> –S 108.3 (109.6). /MW [84]
22	N–C 1.373 (1.357, 1.359), N–N 1.359 (1.351, 1.351), C = C 1.362 (1.387, 1.380), C–C 1.439 (1.422, 1.415), C = N 1.297 (1.325, 1.333), N–H 1.020 (1.002, 0.997); C–N–N 108.9 (113.1, 113.1), C = C–N 107.2 (106.6, 106.3), C–C = C 106.2 (103.7, 104.5), C–C = N 108.1 (112.3, 112.0), C = N–N 109.6 (104.2, 104.1), N–N–H 124.2 (119.6, –). /MW [85], /MW [86]

Abbreviations: MW, microwave; XR, X-ray; ED (gas phase) electron diffraction.

TABLE 7  
CALCULATED AND OBSERVED GAS PHASE DIPOLE MOMENTS

Molecule	$\mu$ [Debye]	
	Calculated	Observed <sup>a</sup>
Water	1.17	1.85
Hydrogen sulfide	0.89	0.97
Ammonia	0.39	1.47
Trifluoromethane	1.98	1.65
Formaldehyde	2.75	2.33
Formic acid	1.82	1.41
Chloromethane	1.39	1.87
Fluoromethane	2.07	1.85
Formaldoxime	0.54	1.31
Dimethylether	1.85	1.30
<i>trans</i> -Acrolein	3.59	3.12
Furan	1.20	0.66
Thiophene	0.37	0.55
Pyrrole	1.87	1.84
Pyridine	1.60	2.19
Chlorobenzene	1.41	1.69
Fluorobenzene	2.12	1.60
Fulvene	0.84	0.42 <sup>b</sup>
Phenol	1.22	1.45
Aniline	1.34	1.53
Toluene	0.41	0.36
Anisole	1.55	1.38
Azulene	1.82	0.80

<sup>a</sup> Values taken from Ref. [40], except <sup>b</sup> from Ref. [87].

produced satisfactorily, except for those compounds drawn in Fig. 1, which shows our computed energies versus the experimental data. As expected, the greatest deviations are observed for

- small condensed ring systems and cyclopropene derivatives,
- compounds which are highly substituted with electron-withdrawing groups ( $>\text{C}=\text{O}$ ,  $-\text{C}\equiv\text{N}$ ,  $-\text{Hal}$ ,  $-\text{O}-$ ),
- compounds with very near non-bonded contacts (*tert*-butyl group, hexamethylbenzene).

Molecular geometries are in good agreement with experiment. The deviations are mostly smaller than 0.03 Å for bond lengths, 4–5 and 10 degrees for bond angles and torsion angles, respectively.

The charge density distributions are comparable to those of *ab initio* methods giving small polarities in the molecular skeleton.

In the presence of high polarities or high strain, the calculated properties (energy, geometry, charge density distribution) are significant within one molecular class: comparisons of absolute values for the properties of interest should be made only for related compounds. Conformational



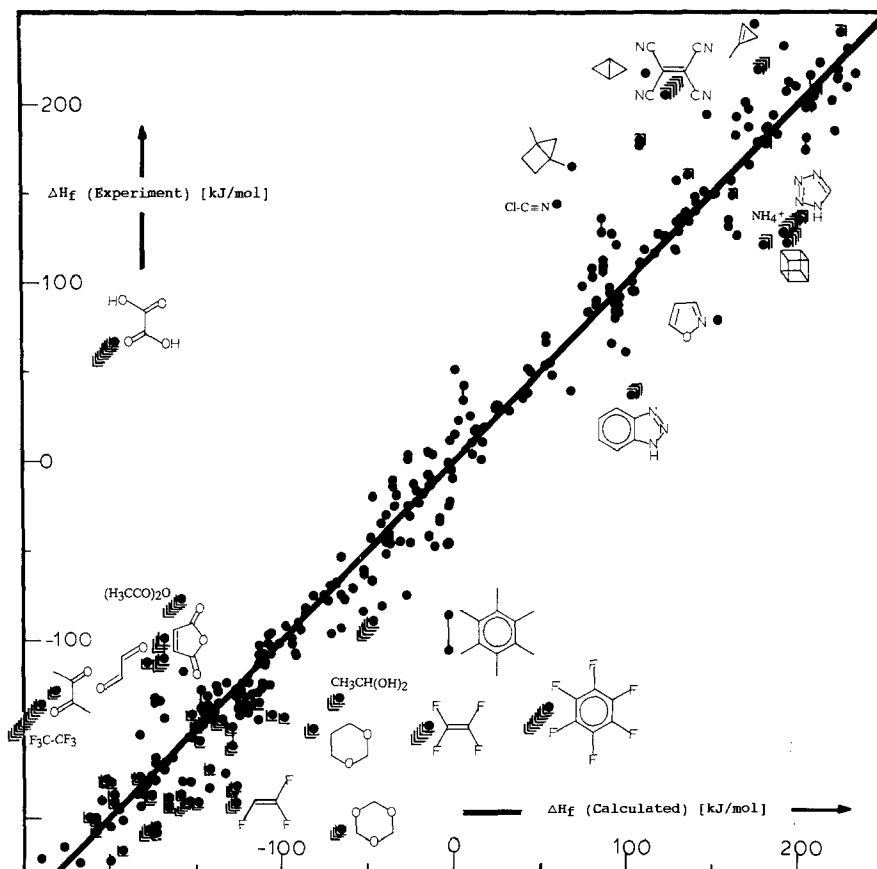


Fig. 1. Experimental and calculated heats of formation. Some of the points were moved along the diagonal into the figure; the arrows give the direction of their original positions [displacement: 100 units per arrow ( $>$ )].

analyses, estimating energy differences for compounds with high flexibility, can be carried out with good accuracy.

## 5 HARDWARE AND SOFTWARE USED

All calculations were run with the FORTRAN version of PIMM on the systems of the Rechenzentrum der Technischen Hochschule Darmstadt: IBM 3090-200 E/VF / MVS-XA 2.2.0 (Zentralrechner) and DEC VAX-8530 / VMS-4.6 (Bereichsrechner 2).

The molecular design was worked out on an IRIS 3120 Workstation / UNIX (Silicon graphics), using both systems PLUTO-78 [41] and MOLCAD [42].

## 6 CONCLUSION

We have developed a procedure to compute molecular geometries, charge densities and conformational energies in three steps:

- $\pi$ -SCF calculation,
- estimation of  $\sigma$ -charge density distribution and
- molecular mechanics with optimization of geometry.

The starting point for the treatment of the  $\pi$ -electronic system was the combined SCF/force field procedure of Lindner [6], whose  $\pi$ -SCF section was based on a valence electrons treatment of Dewar and Harget [43], a forerunner of the widely used MINDO-program [44]. We considered the influence of  $\sigma$ -electrons upon the  $\pi$ -electronic system by the use of simplified CNDO equations [21, 45]. With a  $\sigma$ -dependence of the off-diagonal elements of the  $\pi$ -SCF-matrix, we have been able to strengthen highly polarized or heteronuclear  $\pi$ -bonds, calculating more positive bond orders for them (see the results of methods at a comparable level of accuracy). This was crucial for the correct computation of rotational barriers around bonds with measurable  $\pi$  character, e.g. C–O in carboxylic acids and esters, C–N in amides.

The procedure of Gasteiger and Marsilli [9] for the  $\sigma$ -electronic system was modified to take account of additional polarisations due to the  $\pi$ -SCF-charge density distribution and to the presence of highly strained sites in a molecule.

The original force field [6], working with the gradient method of Murtagh and Sargent [38] for geometry optimization, was extended and reparameterized to include one- and two-centre electrostatic interactions ( $\sigma$ – $\sigma$  and  $\sigma$ – $\pi$ ).

Using only van der Waals and electrostatic potentials, a treatment of hydrogen bonds was worked out to reproduce their gas-phase geometries and energetics.

## ACKNOWLEDGEMENT

We thank the Fonds der Chemischen Industrie for financial support.

## REFERENCES

- 1 See any modern textbook in Organic Chemistry; Lindner, H.J., *Naturwissenschaften*, 61 (1977) 177.
- 2 Náray-Szabó, G., Surján, P.R. and Angyán, J.G., *Applied Quantum Chemistry*, D. Reidel Publishing Company, Dordrecht, 1987; Ahlrichs, R., *Nachr. Chem. Tech. Lab.*, 36 (1988) 738.
- 3 Allinger, N.L., *Adv. Phys. Org. Chem.*, 13 (1976) 1; Burkert, U. and Allinger, N.L., *Molecular Mechanics*, American Chemical Society, Washington, DC, 1982.
- 4 Powell, R.E., *J. Chem. Educ.*, 45 (1968) 558, 790.
- 5 Brickmann, J., *J. Spectrosc.*, 7 (1986) 1.
- 6 Lindner, H.J., *Tetrahedron*, 30 (1974) 1127.
- 7 Lindner, H.J., *Tetrahedron Lett.* (1974) 2479; *Tetrahedron*, 31 (1975) 281; *Tetrahedron*, 32 (1976) 753; *Tetrahedron*, 37 (1981) 535; Lindner, H.J., Hafner, K., Roemer, M. and Kitschke, B., *Liebigs Ann. Chem.*, (1975) 731; Dönges, R., Hafner, K. and Lindner, H.J., *Tetrahedron Lett.*, (1975) 1345; Kessler, H., Ott, W., Lindner, H.J., Schnering, H.G.v., Peters, E.-M. and Peters, K., *Chem. Ber.*, 113 (1980) 90; Stegemann, J. and Lindner, H.J., *Acta Crystallogr.*, B35 (1979) 2161; B36 (1980) 2363; Gleiter, R., Haider, R., Bischof, P. and Lindner, H.J., *Chem. Ber.*, 116 (1983) 3736; Hafner, K., Knaup, G.L., Lindner, H.J. and Flöter, H.-C., *Angew. Chem.*, 97 (1985) 209, 213; Wentrup, C., Mayor, C., Becker, J. and Lindner, H.J., *Tetrahedron*, 41 (1985) 1601; Hafner, K., Knaup, G.L. and Lindner, H.J., *Angew. Chem.*, 98 (1986) 650.
- 8 Lindner, H.J., in Gasteiger, J. (Ed.) *Software-Entwicklung in der Chemie*, Springer-Verlag, Berlin, Heidelberg, 1987, pp 35–41.
- 9 Gasteiger, J. and Marsilli, M., *Tetrahedron*, 36 (1980) 3219.
- 10 Smith, A.E., Dissertation, Technische Hochschule Darmstadt, 1989.

- 11 Egert, E., Universität Frankfurt, Private communication; Program MOMO; Beck, H., Dissertation, Göttingen, 1989.
- 12 Pariser, R. and Parr, R.G., *J. Chem. Phys.*, 21 (1953) 466, 767; Pople, J.A., *Trans. Faraday Soc.*, 49 (1953) 1375.
- 13 Roothaan, C.C., *Rev. Mod. Phys.*, 23 (1951) 69; Hall, G.G., *Proc. R. Soc. London*, A208 (1951) 328.
- 14 Parr, R.G., *J. Chem. Phys.*, 20 (1952) 1499.
- 15 Hinze, J. and Jaffé, H.H., *J. Am. Chem. Soc.*, 84 (1962) 540.
- 16 Parr, R.G. and Snyder, L.C., *J. Chem. Phys.*, 34 (1961) 1661.
- 17 Dewar, M.J.S. and Hojvat, N.L., *J. Chem. Phys.*, 34 (1961) 1232; Ohno, K., *Theor. Chim. Acta* 2 (1964) 219.
- 18 Mulliken, R.S., *J. Chem. Phys.*, 46 (1949) 675; *J. Phys. Chem.*, 56 (1952) 295.
- 19 Slater, J.C., *Phys. Rev.*, 36 (1930) 57.
- 20 Dewar, M.J.S. and Morita, T., *J. Am. Chem. Soc.*, 91 (1969) 796.
- 21 Warshel, A. and Lippicirella, A., *J. Am. Chem. Soc.*, 103 (1981) 4664.
- 22 Heilbronner, E. and Bock, H., *Das HMO-Modell und seine Anwendung*, Vol. 1, Verlag Chemie, Weinheim, 1968, p. 155.
- 23 Carnahan, B., Luther, H.A. and Wilkes, J.O., *Applied Numerical Methods*, Wiley, New York, 1969.
- 24 Del Re, G., *J. Chem. Soc.*, (1958) 4031.
- 25 Mulliken, R.S., *J. Chem. Phys.*, 2 (1934) 782; 3 (1935) 573.
- 26 Pauling, L., *The Nature of the Chemical Bond*, Cornell, Ithaca, New York, 1960; for a current treatise see also: Sen, K.D. and Jorgensen, C.K., (Eds.) *Structure and Bonding*, Vol. 66 (Electronegativity), Springer-Verlag Berlin, 1987.
- 27 Dewar, M.J.S. and Schmeising, H.N., *Tetrahedron*, 5 (1959) 166; 11 (1960) 96; Rademacher, P., *Strukturen organischer Moleküle*, In Klessinger, M. (Ed.), *Physikalische Organische Chemie*, Vol. 2, VCH, Weinheim, New York, 1987.
- 28 Dewar, M.J.S. and De Llano, C., *J. Am. Chem. Soc.*, 91 (1969) 789.
- 29 Warshel, A. and Levitt, M., *J. Mol. Biol.*, 103 (1976) 227.
- 30 Brooks, B.R., Bruccoleri, R.E., Olafson, B.D., States, D.J., Sonaminathan, S. and Karplus, M., *J. Comp. Chem.*, 4 (1983) 187.
- 31 Engler, E.M., Andose, J.D., Schleyer, P.v.R., *J. Am. Chem. Soc.*, 95 (1973) 8005.
- 32 Giglio, E., *Nature (Lond.)*, 222 (1969) 339.
- 33 Kroeker, M. and Lindner, H.J., work currently in progress, Technische Hochschule Darmstadt.
- 34 Mohammad, S.N. and Hopfinger, A.J., *Int. J. Quantum Chem.*, 22 (1982) 1189.
- 35 Hagler, A.T., Huler, E. and Lifson, S., *J. Am. Chem. Soc.*, 96 (1974) 5319.
- 36 Leroy, G., *Adv. Quant. Chem.*, 17 (1985) 1.
- 37 Cox, J.D. and Pilcher, G., *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, 1970.
- 38 Murtagh, B.A. and Sargent, R.W.H., *Computer J.*, 13 (1970) 185.
- 39 Benson, S.W., Cruickshank, F.R., Golden, D.M., Haugen, G.R., O'Neal, H.E., Rodgers, A.S., Shaw, R. and Walsh, R., *Additivity rules for the estimation of thermochemical properties*, *Chem. Rev.*, (1969) 279.
- 40 West, R.C. (Ed.), *CRC Handbook of Chemistry and Physics*, 56th edn., CRC Press, Inc., Cleveland, OH, 1975–1976.
- 41 Motherwell, W.D.S. and Clegg, W., *PLUTO*, Program for Plotting Crystal and Molecular Structures, University of Cambridge, U.K., 1978.
- 42 Brickmann, J. and co-workers, *MOLCAD*, Technische Hochschule Darmstadt, 1987.
- 43 Dewar, M.J.S. and Harget, A.J., *Proc. R. Soc. London*, A315 (1970) 443, 457.
- 44 Dewar, M.J.S., Lo, D.H. and Ramsden, C.A., *J. Am. Chem. Soc.*, 97 (1975) 1311.
- 45 Pople, J.A. and Beveridge, D.L., *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970.
- 46 Corrected for single conformation following: Engler, E.M., Andose, J.D. and Schleyer, P.v.R., (1973) (Ref. [31]).
- 47 Hansen, A.W. and Röhrli, M., *Acta Crystallogr.*, B28 (1972) 2032.
- 48 Boyd, R.H., Sanwal, S.N., Shary-Tehrany, S. and McNally, D., *J. Phys. Chem.*, 75 (1971) 1264.
- 49 Pedley, J.D. and Rylance, J., *Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*, University of Sussex, 1977 (taken from: Leroy (1985); see our Ref. [36]).
- 50 Furukawa, J.I., Sakiyama, M., Seki, S., Saito, Y. and Kusano, K., *Bull. Chem. Soc. Jpn.*, 55 (1982) 3329.
- 51  $\Delta H_f^{298}$  from the heats of combustion in: Zimmermann, H. and Geisenfelder, H., *Z. Elektrochem.*, 65 (1961) 368.
- 52 McCormick, D.G. and Hamilton, W.S., *J. Chem. Thermodyn.*, 10 (1978) 275.
- 53 Derissen, J.L., *J. Mol. Struct.*, 7 (1971) 67.

- 54 Perricaudet, M. and Pullman, A., *Int. J. Pept. Prot. Res.*, 5 (1973) 99; for a theoretical treatment see also: Allinger, N.L. and Chang, S.H.M., *Tetrahedron*, 33 (1977) 1561.
- 55 Subrahmanyam, S.V. and Piercy, J.E., *J. Acoust. Soc. Am.*, 37 (1965) 340.
- 56 Bailey, J. and North, A.M., *Trans. Faraday Soc.*, 64 (1968) 1499.
- 57 George, W.O., Hassid, D.V. and Maddams, W.F., *J. Chem. Soc., Perkin Trans. 2* (1973) 952.
- 58 Nakanishi, H., Fujita, H. and Yamamoto, O., *Bull. Chem. Soc. Jpn.*, 51 (1978) 214.
- 59 Oki, M. and Nakanishi, H., *Bull. Chem. Soc. Jpn.*, 43 (1970) 2558.
- 60 Drakenberg, T. and Forsén, S., *J. Phys. Chem.*, 74 (1974) 1.
- 61 Gáspár, Jr., R. and Gáspár, R., *Int. J. Quantum Chem.*, 24 (1983) 767.
- 62 Drakenberg, T. and Forsén, S., *J. Chem. Soc., Chem. Commun.*, (1971) 1404.
- 63 Jorgensen, W.L. and Swenson, C.J., *J. Am. Chem. Soc.*, 107 (1985) 569.
- 64 Adams, J.W., Geise, H.J. and Bartell, L.S., *J. Am. Chem. Soc.*, 92 (1970) 5013.
- 65 Oberhammer, H. and Bauer, S.H., *J. Am. Chem. Soc.*, 91 (1969) 10.
- 66 Traetteberg, M., *Acta Chem. Scand.*, 20 (1966) 1724.
- 67 Bordner, J., Parker, R.G. and Stanford, Jr., R.H., *Acta Crystallogr.*, B28 (1972) 1069.
- 68 Chiang, J.F. and Bauer, S.H., *J. Am. Chem. Soc.*, 92 (1970) 261.
- 69 Beagley, B. and Hewitt, T.G., *Trans. Faraday Soc.*, 64 (1968) 2561.
- 70 Larsen, N.W., *J. Mol. Struct.*, 51 (1979) 175.
- 71 Lister, D.G., Tyler, J.K., Hoeg, J.H. and Larsen, W., *J. Mol. Struct.*, 23 (1974) 253.
- 72 Banerjee, A., *Acta Crystallogr.*, B29 (1973) 2070.
- 73 Lahiri, B.N., *Acta Crystallogr.*, A25 (1969) 127.
- 74 Kitano, M. and Kuchitsu, K., *Bull. Chem. Soc. Jpn.*, 46 (1973) 3048.
- 75 Ottersen, T. and Almlöf, J., *Acta Crystallogr.*, B36 (1980) 1147.
- 76 Sugie, M. and Kuchitsu, K., *J. Mol. Struct.*, 20 (1974) 437.
- 77 Kitano, M., Fukuyama, T. and Kuchitsu, K., *Bull. Chem. Soc. Jpn.*, 46 (1973) 384.
- 78 Iley, R.C. and Davis, M.I., *J. Chem. Phys.*, 57 (1972) 1909.
- 79 Laurie, V.W., *J. Chem. Phys.*, 34 (1961) 291.
- 80 Sadova, N.I., Vilkov, L.V. and Anfimova, T.M., *Zh. Strukt. Khim.*, 13 (1972) 763.
- 81 Soerensen, G.O., Mahler, L. and Rastrup-Andersen, N., *J. Mol. Struct.*, 20 (1974) 119.
- 82 Werner, W., Dreizler, H. and Rudolph, H.D., *Z. Naturforsch.*, 22a (1967) 531.
- 83 Stiefvater, O.L., *J. Chem. Phys.*, 63 (1975) 2560.
- 84 Nygaard, L., Amussen, E., Hoeg, J.H., Maheshwari, R.C., Nielsen, C.H., Petersen, I.B., Rastrup-Andersen, J. and Soerensen, G.O., *J. Mol. Struct.*, 8 (1971) 225; 9 (1971) 220.
- 85 Nasibullin, R.S., Latypova, R.G., Troitskaya, V.S., Vinokurov, V.G. and Pozdeev, N.M., *Zh. Strukt. Khim.*, 15 (1974) 47.
- 86 Nygaard, L., Christen, D., Nielsen, J.T., Pedersen, E.J., Snerling, O., Vestergaard, E. and Soerensen, G.O., *J. Mol. Struct.*, 22 (1974) 401.
- 87 Baron, P.A., Brown, R.D., Burden, F.R., Domaille, P.J. and Kent, J.E., *J. Mol. Spectrosc.*, 43 (1972) 401.