MASTER

DEVELOPMENT OF EMPIRICAL POTENTIAL FUNCTIONS FOR THE STUDY OF
MOLECULAR GEOMETRY, AND APPLICATIONS TO CHLOROPHYLL A DIMERS

by

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PROLOGUE

A purpose of the present studies is twofold: (1) development of an empirical potential function (EPF) and (2) application of it to the studies of photoreaction center chlorophyll a dimer.

The reliable estimate of geometric structures and energies of large molecules by quantum mechanical methods is not possible at the present time. An alternative method is, therefore, needed for the studies of large molecular systems, and Chapter I is dedicated to the development of this tool, i.e., an empirical potential function, which could suffice this purpose. Because of a large number of variable chemical compositions and functional groups characteristically present in a large molecule, it is important to include a large number of structurally diverse molecules in the development of the EPF.

In Chapter II, the EPF is applied to study the geometrical structure of a chlorophyll a (Chl a) dimer, which is believed to exist at the photoreaction center of green plants and is known to play an essential role in photosynthetic energy conversion. Although various models have been proposed for this dimer structure, there is still a great need for information concerning the detailed geometric structure of this dimer. Therefore, in this chapter the structural stabilities of various dimer models are examined by the EPF, and detailed and quantitative information on the structure and stability of these models is provided.

I. DEVELOPMENT OF EMPIRICAL POTENTIAL FUNCTIONS
FOR THE STUDY OF MOLECULAR GEOMETRY.

Introduction

Despite the help of high speed electronic computers and advances in techniques, the reliable estimate of geometric structures and relative energies of molecules having large numbers of geometric degrees of freedom by quantum mechanical methods is not possible at the present time. In this regard, a method using an empirical potential function represents a useful approach to a solution of this problem, and has been used quite successfully in many areas.¹

Much of the literature dealing with empirical potential functions, however, is focused on applications directed toward a specific problem or class of molecules,² and applications to molecular systems having large geometrical degrees of freedom and variable chemical composition are usually accompanied with partial and/or total neglect of intra-molecular interaction terms in the potential function.

Therefore, our present goal is to obtain an empirical potential function which is applicable to a wide variety of organic molecules, and which provides an adequate representation of both intra- and inter-molecular interactions.

Description of the Empirical Potential Function

The total energy (E) of a molecule is partitioned into seven components, i.e.,

$$E = E^b + E^{ang} + E^{op} + E^{tor} + E^{nb} + E^{hb} + E^{el} \quad (1)$$

where the energies are in units of kcal/mol, and the formula for each term is described below. All lengths (distances) are measured in Å and all angles in degrees. The numerical constant appearing directly to the right of each sign ("=") in the formulas for individual terms is a conversion factor which properly scales the results to the appropriate energy units, i.e., kcal/mol.

The first four terms in eq. (1) are intramolecular terms, and describe essentially all of the important intramolecular motions of a molecule (i.e., bond stretching, angle bending, out-of-plane bending, and internal rotation around a bond). However, no cross terms corresponding to coupling between these intramolecular motions are included, since the contributions of these terms to a total energy are expected to be relatively small, and the number of parameters would be increased enormously by this inclusion. The first three terms in eq. (1) are represented by harmonic functions alone, since our potential function is designed to predict the equilibrium molecular structures, and applications to non-equilibrium structures such as transition states or dissociation processes are not considered. Because of the nature of the motion (internal rotation), the fourth term is described by a periodic function.

The last three terms in eq. (1) are used to describe the interactions between atoms which are not bonded, and may include both intra- and intermolecular interactions.

The bond deformation energy (E^b) is given by

$$E^b = \sum_{i,j} E_{ij}^b = 71.985 \sum_{i,j} f_{ij}^b [r_{ij} - r_{ij}^{(0)}]^2, \quad (2)$$

where r_{ij} is the bond distance between atom i and atom j , f_{ij}^b is the stretching force constant (in mdyne $\text{\AA}^{-1}$) associated with the bond between atoms i and j , and $r_{ij}^{(0)}$ is the equilibrium bond distance. The sum is taken over all bonds, and f_{ij}^b and $r_{ij}^{(0)}$ are the parameters to be chosen.

The angle deformation energy (E^{ang}) is given by

$$E^{\text{ang}} = \sum_{ijk} E_{ijk}^{\text{ang}} = 0.021926 \sum_{ijk} f_{ijk}^{\theta} [\theta_{ijk} - \theta_{ijk}^{(0)}]^2. \quad (3)$$

The sum is taken over all ijk in which there is a bond between atom i and atom j , and a bond between atom j and atom k , f_{ijk}^{θ} is the bending force constant (in mdyne/rad²) associated with the angle θ_{ijk} , and $\theta_{ijk}^{(0)}$ is the equilibrium bond angle. f_{ijk}^{θ} and $\theta_{ijk}^{(0)}$ are the parameters to be chosen.

The out-of-plane energy (E^{op}) is given by

$$E^{\text{op}} = \sum_{\ell} E_{\ell}^{\text{op}} = \sum f_{ijk\ell}^{\text{op}} d^2. \quad (4)$$

The sum is taken over all sp^2 planar hybridized carbon atoms (ℓ), and d is the distance of atom ℓ from the plane of atoms i, j, k bonded to atom ℓ . $f_{ijk\ell}^{\text{op}}$ is the force constant (in kcal/mol $\text{\AA}^2$) associated with out-of-plane bend around the sp^2 nucleus, and is the parameter to be chosen.

The torsional strain energy (E^{tor}) is given by

$$E^{\text{tor}} = \sum_{ijk\ell} E_{ijk\ell}^{\text{tor}}, \quad (5)$$

where

$$E_{ijkl}^{\text{tor}} = U_{ijkl} [1 + g_{ijkl} \cos(h_{ijkl} \phi_{jk})] + U'_{ijkl} [1 + g'_{ijkl} \cos(h'_{ijkl} \phi_{jk})]. \quad (6)$$

The sum is taken over all dihedral angles ϕ_{jk} in which there are bonds between atoms i and j , j and k , and k and l . U_{ijkl} (U'_{ijkl}) is the torsional barrier height, h_{ijkl} (h'_{ijkl}) is the periodicity of the barrier and g_{ijkl} (g'_{ijkl}) is the sign (either plus or minus). These six constants are the parameters to be chosen. The dihedral angle is defined as an angle made of vectors, each of which is perpendicular to a vector $j-k$, and lies in the planes $i-j-k$ and $j-k-l$, respectively. A positive dihedral angle is measured in a clockwise direction from a vector lying in the plane $i-j-k$ to a vector lying in the plane $j-k-l$.

The non-bonded interaction energy (E^{nb}) is given by

$$E^{\text{nb}} = \sum_{ij} E_{ij}^{\text{nb}}, \quad (7)$$

where

$$E_{ij}^{\text{nb}} = a_{ij} e^{-b_{ij} r_{ij}} - c_{ij} / r_{ij}^6, \quad (8)$$

where ij includes all pairs of atoms i , j that are separated by more than two bonds, r_{ij} is the distance between atoms i and j , and a_{ij} , b_{ij} , and c_{ij} are the parameters to be chosen.

An (exp-6) potential was chosen to describe this part of the interatomic interaction potential because the London dispersion energy has an inverse sixth-power dependence on the interatomic distance, and studies³ of repulsion between small molecules (e.g., He..He, H₂..H₂) indicate that the exponential form gives the most accurate description of the non-bonded repulsion.

The hydrogen bond energy (E^{hb}) is given by

$$E^{hb} = \sum_{ij} E_{ij}^{hb}, \quad (9)$$

where

$$E_{ij}^{hb} = a'_{ij} e^{-b'_{ij} r_{ij}} - c'_{ij}/r_{ij}^6, \quad (10)$$

where the subscript i refers to the hydrogen atom bonded to the donor atom and j to the acceptor atom. r_{ij} is the distance between atoms i and j , and a'_{ij} , b'_{ij} , and c'_{ij} are the parameters to be chosen.

In the case where a H atom and an acceptor atom are included in the summation of Eq. (9), these atoms are excluded from the summation in Eq. (7). For convenience in computation, the same functional form (exp-6) as in the non-bonded interaction potential was used. Eq. (9) was used when the distance between the donor and acceptor was shorter than a threshold distance and Eq. (7) was used otherwise. The value of the threshold distance was chosen in such a way that this

distance is long enough to ensure that no hydrogen bond would be expected to occur beyond this distance (i.e., a distance much longer than the observed donor-acceptor distance) and at the threshold distance there is a smooth transition between the non-bonded interaction and hydrogen bond potential functions. For example, a value of 3.3 Å was chosen for the threshold distance in the hydrogen bond O-H...O.

The electrostatic interaction energy (E^{el}) is given by

$$E^{el} = \sum_{ij} E_{ij}^{el} = \sum_{ij} 332.0 Q_i Q_j / (D r_{ij}) \quad (11)$$

The sum is taken over all pairs of atoms i, j separated by more than two bonds, r_{ij} is the distance between atoms i and j and a parameter D is the effective dielectric constant to be chosen.

The partial charges Q_i, Q_j (in electronic units) are selected to reproduce the observed electric dipole moments of the molecules, and detailed procedures to obtain the partial charges will be discussed later. When formal charges (two or more) are present, only the actual charges ($\pm N$, where N is an integer) are used.

Procedures for Parameter Choice

The procedure for parametrization is shown in Figure 1 in a simplified way by a flow chart. In Figure 2 are listed molecules which were used for parametrization and testing of the intramolecular interaction potential functions, and molecules used for testing intermolecular

interactions (i.e., E^{nb} and E^{el}) are given in Figure 3. In Table 1, code numbers are listed which designate the various types of C and N atoms (e.g., primary sp^3 hybridized carbon, primary sp^3 hybridized nitrogen, etc.). Although the parameters in the various components in Eq. (1) are interrelated to each other to varying degrees, it was found to be a fairly good initial approximation to choose the parameters from various independent sources, and then successively modify these when necessary to achieve an acceptable fit to the available experimental data. A more detailed description of the parametrization procedure for each energy component is described below.

(1) Parameters for E^b , E^{ang} , E^{op} :

As initial choices, the bond stretching and angle bending force constants, f_{ij}^b and f_{ijk}^θ , respectively, were obtained from literature values⁴ based on vibrational analyses. The parameters $r_{ij}^{(0)}$ and $\theta_{ijk}^{(0)}$ were set equal to the experimental values obtained in the gas phase, since the gas phase data are more accurately measured than the crystal data (see a more detailed discussion in the Discussion Section). Force constants not available in the literature were taken to be equal to the literature values of the closest bond and angle analogs.

With these values as the initial parameters, the minimum energy conformation of a molecule was calculated by minimizing the total energy with respect to the coordinates of atoms, and then the calculated bond lengths and angles were compared with the experimental values. This procedure (see flow chart in Fig. 1) was repeated by changing the parameters until agreement with the observed molecular structure was obtained,

and wherever possible the gas phase data were used for refinement of the parameters. An agreement was considered satisfactory when the calculated values agreed within $\sim 1\%$ for bond length and within $\sim 2\%$ for bond angles of the observed values. In the evaluation of the total energy, all of the energy components were used at this stage except the electrostatic interaction term (E^{el}), since inclusion of E^{el} gave no appreciable changes in the calculated bond lengths and angles on the calculations of several molecules (*i.e.*, 20 molecules representing each class of molecules such as alkanes, alcohols, esters, acids, etc.).

In the energy minimization, the pattern-search method⁵ was used throughout this study except that the method of Davidon and Fletcher⁶ was employed in the crystal packing calculation (to be discussed later).

E^{op} is used only for sp^2 hybridized C atoms, and the value of $100.0/\text{kcal mol } \text{\AA}^2$ was arbitrarily assigned for the force constant. This value was chosen to be large enough to ensure planarity around the C atom after the energy minimization, but not so large that E^{op} completely outweighs the other energy components at the start of minimization and prohibits out-of-plane bending at the C atom for some highly constrained molecules where there is a deviation from planarity (*e.g.*, see molecule 134 in Fig. 2).

The parameters thus chosen for E^{b} and E^{ang} are listed in Tables 1 and 2, respectively. It was necessary to specify the types of atoms in the parameters of E^{b} and E^{ang} , rather than just considering the atoms directly involved, since the bond lengths and angles are affected by the nearest neighboring groups, the effect of which can be introduced into E^{b} and E^{ang} through these parameters. A cross term (*i.e.*, a

coupling between bond stretching and angle bending) neglected in Eq. (1) can also be indirectly or partially taken into account by these parameters.

(2) Parameters for E^{tor} :

The periodicity $h_{ijkl}(h'_{ijkl})$ was chosen on the basis of symmetry considerations of individual molecules, and the value 1, 2 or 3 was used in all cases studied here. The sign $g_{ijkl}(g'_{ijkl})$ was chosen so as to reproduce the correct positions of observed energy minima (e.g., cis, trans or gauche forms). The value of the barrier height $U_{ijkl}(U'_{ijkl})$ was taken from the experimental barrier height.⁷ With these parameters the total energy was evaluated at several dihedral angles to calculate the barrier height and energy difference between the conformers, and then a comparison was made with experimental data. Gas phase data were used in most cases, but the data measured in solution were used when gas phase data were unavailable (e.g., for HCO-OCH_3).

Because of the effect (non-bonded repulsion) of E^{nb} on internal rotation, the parameter $U_{ijkl}(U'_{ijkl})$ was modified so as to reproduce the observed barrier height, when necessary, through this calculation.

The barrier height was calculated in two different ways, i.e., by rigid rotation where the bond lengths and angles are not allowed to change during the internal rotation, and by an adiabatically relaxed rotation where the total energy was minimized with respect to all other degrees of freedom at each fixed dihedral angle, thereby allowing possible distortions of the geometry during the rotation.

In the rigid rotation, the positions of energy minima were found

correctly in most of the small molecules, but for some molecules with two or more energy minima (e.g., butadiene and esters) the barrier heights were difficult to calculate correctly due to repulsive non-bonded interactions, thus making the refinement of $U_{ijkl}(U'_{ijkl})$ difficult. This problem is, however, removed in the adiabatically relaxed rotation.

For the parameters $U_{ijkl}(U'_{ijkl})$ for which experimental barrier heights are unavailable, it was necessary to estimate these quantities by analogy to their closest analogs. The parameters in E^{tor} are given in Table 4, where the code numbers are used to designate the various types of C and N atoms.

Transferability of the parameters of E^b and E^{ang} was tested for as many molecules as possible, and over 140 molecules (see Fig. 2) were used for the parametrization and test of these intramolecular potential functions, including E^{op} and E^{tor} as well. It is worthwhile to mention at this point that there is nothing unique about the values of the various parameters chosen, except that they work well, i.e., the experimental data can be well reproduced.

In Figure 2, the letters b, a, o, and t appearing to the right side of the molecule refer to the molecules, which were used for parametrization of these intramolecular terms E^b , E^{ang} , E^{op} and E^{tor} , respectively. It should be remembered, however, that these molecules may be referred to in terms of the individual parameters (e.g., parameters for C-C, C=C, C-C-C, C=C-C, etc.), since the same molecule was used for parametrization of one or more parameters (e.g., for C-C or C=C-C) and also for the test of other parameters (e.g., for C=C or C-C-C) at the same time.

(3) Parameters for E^{el} :

The electrostatic dipole moment of a molecule is assumed to be a vector sum of the bond moments $\underline{m}_i$'s (in Debyes) assigned to each bond and acting as the vectors along the lines of the bonds.

The partial charge Q_X (in electronic units) of the atom X is defined as

$$Q_X = \sum_i q_{X_i}, \quad (11-a)$$

where

$$q_{X_i} = \pm |\underline{m}_i| / 4.803 |\underline{l}_i|, \quad (11-b)$$

where $\underline{l}_i$ is a vector coincidental with bond i and has a magnitude equal to the bond length, and the sign is determined by the relative electronegativity of the two atoms making the bond i . The sum is taken over all of the bonds i 's associated with atom X, and $|\underline{m}_i|$ is regarded as a transferable constant. Transferability of this constant can be tested by comparing the calculated dipole moments with the observed ones for various types of molecules. For the value of $|\underline{l}_i|$, the experimental bond distance was used. Most of the values (listed in Table 5) of $|\underline{m}_i|$'s were taken from the literature,⁸ and a modification was made for the bond moment of the carbon-carbon double bond present in some molecules (i.e., pyrrole, furan and related molecules).

For the following reasons, a method using the bond moment was adopted to obtain the partial charge rather than a quantum mechanical method.

First, the calculated value of the partial charges by the latter method varies depending on the basis set that is used. For example, the calculated partial charge of the O atom of water is -0.406 with a STO-3G basis set^{9a} and -0.772 with a double zeta basis set^{9b} (see references 9a and 9b for other examples).

Secondly, the calculated electric dipole moment by the former method gives better agreement with the observed dipole moment than the one by the latter method (see Table 6).

With partial charges obtained from bond moments, the total energy was minimized, and then the dipole moment of the molecule was calculated. The results for several molecules are listed in Table 6 along with those of ab initio SCF calculations.

It is difficult to make a reliable estimate of the magnitude of the effective dielectric constant D , since it depends not only on the distance between the charges but also the surrounding environment (e.g., solvent molecules). A value of 3.0 was selected after examining the effect of variation in D on geometry minimization and crystal packing calculations (discussed in a later section), and values in the range from 1.0 to 4.0 gave no significant effects on the results of these calculations.

(4) Parameters for E^{nb} :

The parameters involving atoms H, C, N, and O in E^{nb} are taken with some modifications^{10a} from the literature^{2b,10} and are listed in Table 7.

These parameters were derived from crystal packing calculations

on small molecules where the lattice (i.e., crystal) energy of the molecular crystal is represented by a non-bonded interaction potential of the same form as in Eq. (7), and the parameters are chosen so as to reproduce the heats of sublimation and the lattice constants of a unit cell. The above references should be consulted for details of the parametrization.

In order to provide a further test of these parameters, crystal packing calculations were done for 18 molecules (see Fig. 3) by the procedure¹¹ described below, and the results of the calculated crystal energies E_{cr} and lattice constants ($a, b, c, \alpha, \beta, \gamma$) are given in Table 8.

The crystal energy E_{cr} is expressed as a sum of non-bonded (Eq. 7) and electrostatic (Eq. 11) interactions between a central molecule and the surrounding molecules, and all the molecules are treated as rigid bodies. E_{cr} is then minimized with respect to lattice constants.

The Cartesian coordinates of the central molecule are taken from the crystal data, and the other molecules are generated from the central molecule using rotational (R) and translational (S and N) operators,¹¹ i.e.,

$$\underline{x}_{qn}^t = \underline{D} \underline{R} \underline{D}^{-1} \underline{x}_{p0}^t + \underline{D}(\underline{S} + \underline{N}) , \quad (12)$$

where the vector $\underline{x}_{p0}^t$ represents the cartesian coordinate of the t-th atom of the p-th (central) molecule in the 0-th unit cell, and $\underline{x}_{qn}^t$ the Cartesian coordinate of the t-th atom of the q-th molecule in the n-th unit cell.

D is the matrix operator which converts the fractional coordinates

into the Cartesian coordinates and is a function of the lattice constants. The rotational operator $\underline{R}$ orients each molecule relative to the central molecule. The translational operator $\underline{S}$ positions the center of mass of the other molecules in the 0-th unit cell relative to the central molecule (in the 0-th unit cell), and is taken as a fraction of the unit cell axis. The translational operator $\underline{N}$ is a vector with integer components which extends in principle from $-\infty$ to $+\infty$, and generates all lattice sites (i.e., all unit cells).

The translational and rotational operators are defined uniquely by the crystal symmetry, and are not allowed to change as the lattice constants are varied during energy minimization. Furthermore, only those lattice constants whose change does not affect the crystal symmetry are allowed to vary in the minimization process. For example, in a monoclinic crystal where $\alpha=90$, α is not allowed to change during minimization, since an alteration of α would change the crystal symmetry.

The number of unit cells taken along each axis is such that the distance from the central molecule to the edge of the crystal was generally greater than 10 Å in both directions along each axis. No appreciable differences were seen in the calculated lattice constants and crystal energy when the size (specified by cell index in Table 8) of the microcrystal was increased. For example, when the number of molecules in the microcrystal was increased from 175 (i.e., cell index 557) to 395 (i.e., cell index 757) in the calculation of p-benzoquinone, the crystal binding energy was increased by only 0.02 kcal/mol, and the changes in the lattice constants were much smaller than the experimental errors in these constants.

Minimization was terminated after the magnitude of the first derivative of the energy with respect to each variable was smaller than 0.001 kcal/mol Å and 0.001 kcal/mol rad.

(5) Parameters for E^{hb} :

The hydrogen bond systems considered here are those where the donor groups have hydroxyl groups (i.e., water and alcohol), and the acceptor groups have carbonyl groups (i.e., aldehyde, ketone and ester). Systems involving carboxylic acids are not included, but parameters could be added if needed.

The only experimental data available for these systems are heats of dimerization in solution.^{12a} No experimental data concerning the O..O distance are available except ab initio SCF calculations on the systems $\text{H}_2\text{O}..\text{O}=\text{CH}_2$ ^{12b,c} and $\text{MeOH}..\text{O}=\text{CH}_2$.^{12b} Thus, the parameters, a' , b' , c' , were chosen so as to reproduce the O..O distance obtained by ab initio SCF calculations and the heat of dimerization; the resulting values are 161,758.0 (kcal/mol), 6.0 (Å⁻¹) and 228.3 (kcal Å⁶/mol), respectively.

The calculated hydrogen bond energy corresponding to a hypothetical motionless state at 0 °K should be larger in general than the heat of dimerization measured around room temperature, since the hydrogen bonding is expected to be weaker at higher temperature. This temperature dependence of the hydrogen bond energy is attributed to the thermal motions of the molecules, and no correction for the calculated energy due to the thermal motions was made. Although a reliable estimate of this correction is difficult, a rough estimate of as much as 1.2 kcal/mol

at room temperature is obtained from the following consideration. In going from two monomer molecules to a dimer, three degrees of translational and three degrees of rotational freedom are lost, each of which contributes $(1/2)RT$. There is also a gain of six degrees of intermolecular vibrational freedom, which will contribute $6RT$, assuming that the vibrations occur at low frequencies. The total effect will, therefore, amount to $2RT$ (1.2 kcal/mol at room temperature), allowing for the contribution of $-RT$ from $\Delta(PV)$. The effect due to the changes in intramolecular vibrational frequencies is therefore not taken into account, since these changes are expected to be small at room temperature.

Discussion and Summary

Discussion of the geometry and energy calculations will be followed below.

Geometry:

In Tables 9 and 10 is given a summary of the calculated bond lengths and angles for a wide variety of structurally diverse molecules. The parameters were chosen so as to reproduce gas phase data, and in most cases the agreements obtained are within $\sim 1\%$ for the bond lengths and within $\sim 2\%$ for the bond angles. In the parametrization, the gas phase data were preferentially used for comparison whenever possible for the following reasons:

The molecular structure in the crystal is subject to various influences, such as intermolecular forces, crystal packing effects, and the presence of anions or cations (e.g., C^- , Br^- , Na^+ , etc.). There-

fore, the geometry found in the crystal usually differs from that in the isolated state (i.e., gas phase). These environmental effects on the molecular structure are, however, extremely difficult to estimate, and are not taken into account explicitly in our potential function except that the intermolecular interaction is implicitly incorporated in the non-bonded interaction parameters which are obtained from the crystal packing calculations. Besides these effects, X-ray diffraction data are generally much less accurate than the gas phase data, and the temperature at which the X-ray diffraction is usually carried out also affects the molecular structure. In general, these factors affecting the molecular crystal structure are reflected in large deviations in the bond lengths and angles compared to those in the gas phase.

A more detailed discussion on the calculated bond lengths and angles will be given below for each class of molecules, and those molecules in which a large error was found (molecules in crystal in most cases) will be discussed separately.

A. Hydrocarbons:

The errors in C-C bond lengths are, in most cases, within $\sim 1\%$ of both the gas phase (0.6% on average out of 34 molecules) and crystal data. A relatively large error (2.6%) in the strained molecule cyclobutane (molecule 7 in Fig. 2 or Mol 7) is probably due to limitations of our potential function, and the observed bond length (1.57 Å) is considerably longer than those in other alkanes (hereafter each molecule will be referred to by the number used in Fig. 2). The large error (4.2%) in the C-C bond length of the cyclobutane ring of

Mol 99 (i.e., see bond b in Fig. 2) is also ascribed to the limitations of the potential function.

The C=C bond lengths of conjugated systems show relatively large errors compared with those in the isolated C=C bonds (e.g., 1.5, 2.2, 1.4 and 1.3%, in Mols 21, 23a, 23b and 99, respectively), since the C=C bond parameters obtained from isolated C=C bonds are used, and the effect of conjugation is not taken into account in the calculation by any means. The average error in calculated C=C bond lengths compared to gas phase data is 0.5% for 23 molecules.

A considerably shorter C=C bond length (1.314 Å) is observed for ethylene (Mol 14) by X-ray diffraction methods at 85°K, and reflects the effect of temperature, being shorter by ~ 0.02 Å than the bond length observed in the gas phase. This shrinking in bond lengths is observed in most of the X-ray data in Table 9. The degree of this shrinking due to thermal motion is, however, difficult to estimate in general, since the experimental accuracy in X-ray diffraction is usually of about the same order.

A rather detailed analysis for this thermal motion of benzene (Mol 10) in the solid state was made by Cox^{13a} in the X-ray study (at -3° C), where the observed C=C bond length (1.378 Å) was found to be significantly shorter than the one (1.397 Å) obtained by high resolution Raman spectroscopy,^{13b} and correction for this thermal motion was calculated to be approximately 0.015 Å.

The errors in the CCC bond angle are in most cases within 2% of both the gas phase (0.9% on average out of 28 molecules) and crystal data. The large errors (more than 3.5%) found in Mols 80 and 81 are

most likely due to experimental inaccuracies, since both molecules are quite large (89 atoms), and the resolution of the X-ray diffraction for this size of molecules is generally not expected to be high enough to give accurate location of all atoms. This low accuracy in the X-ray data is also seen in the considerably short C=C bond lengths (1.316 and 1.297 Å for Mols 80 and 81, respectively) compared with the normal C=C bond length (~ 1.34 Å).

B. Amines:

Most of the data for the amines studied here are from solid state experiments and the errors in the C-N bond lengths are within 1.5% of both gas phase (0.9% on average out of 6 molecules) and crystal data. The errors in the C-N bond lengths of Mols 34 (2.6%) and 130 (2.4%) are ascribed to experimental inaccuracies, where the estimated deviations in the bond lengths are 0.01 Å (Mol 34) and 0.03 Å (Mol 130). The relatively large errors (up to 2.2%) in most of the aromatic C=N double bonds are partially ascribed to limitations of the potential function, since the same bond parameters were used for both five- and six-membered ring molecules.

Errors in acyclic C=N=C, aromatic C=N=C and aromatic C=C=N bond angles are in most cases within 1.5% of both the gas phase (0.2% on average for 4 molecules) and crystal data. Relatively large errors (up to 2.7%) are seen in some of the C-N-C angles (e.g., Mol 112), all of which are in five-membered cyclic rings. These errors are partially due to the parametrization of the bond angles where both the C-N-C and adjacent C=C-N bond angles had to be taken into account during the

parametrization, and the errors in the latter bond angles are within 1.5% of the observed ones.

The largest errors in bond angles are seen in the C-C-N⁺ bond angles where the N⁺ is a quaternary nitrogen, and are attributed to the presence of anions present in the crystal. The errors (2.9-9.3%) in the C-C-N⁺ bond angles of Mol 74 are due to the hydrogen bond through the N⁺ cation and Cl⁻ anion present in the crystal which brings about considerably distortion of the bond angles. The error (4.7%) in the C-C-N⁺ bond angle of Mol 73 is due to a combination of low accuracy of the X-ray diffraction (estimated deviation of 2° in the bond angle) and the presence of the I⁻ anion in the crystal.

C. Alcohols, ethers and esters:

The errors in the C(alkyl)-O bond lengths of alcohols, ethers and esters are within 1.5% (0.6% on average for 10 molecules) of the observed gas phase data and, in most cases, within 2.0% of the crystal data. The largest errors (3.7%) in the C-O bond lengths are seen in Mols 30 (ester) and 83 (alcohol), and are most likely due to experimental inaccuracies in the X-ray diffraction data, since the size of these molecules (83 and 132 atoms for Mols 30 and 83, respectively) is quite large, and the observed bond lengths (1.491 and 1.495 Å for Mols 30 and 83, respectively) are unusually long compared with other C-O bond lengths (see MW data 1.437 Å and 1.425 Å of Mols 29 and 35 for ester and alcohol, respectively).

The C=O and C(=O)- bond lengths and C-C=O bond angles of esters will be discussed in Section D.

The errors in C-C-O bond angles of alcohols and ethers are within ~2% of the gas phase (1.7% on average out of 3 molecules) and crystal data.

The largest errors (more than 4%) are seen in the C-C(tertiary)-O bond angles in Mols 54, 56, 57 and 76. In Mol 76, the Ag^+ cation present in the crystal makes a considerable distortion (see errors 4.9 and 6.0%) of the C-C-O bond angles through the $\text{Ag}^+ \cdots \text{O}$ interaction. In Mol 54, the error (6.2%) is attributed to the Cl^- anion present in the crystal which makes the hydrogen bond $\text{O}-\text{H} \cdots \text{Cl}^-$, thereby causing the distortion of the C-C-O bond angle. The errors (4.4 and 4.1% in Mols 56 and 57, respectively) are possibly due to the hydrogen bond of the type $\text{O} \cdots \text{H}-\text{C}$ where the C-H is in the methyl group bonded to quaternary N^+ , since the observed distances of $\text{O} \cdots \text{C}$ are 2.90 and 2.95 Å in Mols 56 and 57, respectively, which are considerably shorter than the van der Waals distance (3.1 Å) between the atoms O and C.

The errors in the C-O-C bond angles are in most cases within 2.5% of both the gas phase (1.4% on average for 7 molecules) and crystal data. Agreement of the calculated C-O-C bond angles with the microwave data of Mols 96 (1.8%) and 98 (2.4%) should be regarded as satisfactory, since the parameters of these bond angles are used for a wide range of bond angles, i.e., from ~111° (e.g., Mols 96 and 97) to ~120° (e.g., Mols 51 and 110).

D. Aldehydes, ketones and acids:

The errors in the ester $\text{C}(=\text{O})-\text{O}$ bond lengths are within 2.5% of both the gas phase (gas phase data are available only for methyl formate, Mol 29) and crystal data, except for an error (3.6%) in Mol 30,

which is most likely due to experimental inaccuracy, since the observed data were taken from the ester group of methyl pheophorbide (83 atoms).

Quite large errors (3.3-7.3%) are seen in the C(=O)-O bond lengths of some carboxylic acids (i.e., Mols 32, 82, 86, 90 and 94), and in all of these molecules the bond lengths in the crystal are quite short (less than ~ 1.32 Å) compared to the gas phase data (e.g., 1.343 and 1.361 Å of formic acid in MW and Ed data, respectively). The most probable explanation for this is that the carboxylic group C(=O)-O has a partially ionized form similar to a carboxylate anion $\text{O}^+=\text{C}=\text{O}^-$ due to the hydrogen bonding O-H...O(=C) present in the crystal.

The errors in C(-O)=O bond lengths of acids and esters are within 2% of the gas phase data (1.3% on average for 3 molecules) and in most cases within 2.5% of the crystal data.

The relatively large errors in Mols 30 (3.2%), 34 (3.8%) and 130 (4.9%) are due to experimental inaccuracies of the X-ray diffraction data, where the estimated deviations in the bond lengths for these molecules are 0.01, 0.01, and 0.03 Å, respectively.

Unlike the carboxylic C=O bond lengths, the errors in the carbonyl C=O bond lengths of aldehydes and ketones are much smaller and within 1.5% of both the gas phase (0.7% on average for 6 molecules) and crystal data, except those of Mols 85 (5.6%) and 87 (3.1%). The errors in these two molecules are due to experimental inaccuracies due to the molecular sizes (59 and 85 atoms, for Mols 85 and 87, respectively), and the observed bond lengths (1.16 and 1.19 Å for Mols 85 and 87, respectively) are significantly short compared with ~ 1.22 Å, the value found in gas phase data of the other molecules. In Mol 87, large errors

of 3.6 and 4.9% are also seen in the C=C and C(=C)-C(methyl) bond lengths, respectively, both of which are considerably shorter than the normal bond lengths found in the other molecules.

The errors in C-C(=O) bond lengths of aldehydes and ketones are within 0.5% of the gas phase data (0.3% on average for 3 molecules) and within 1.5% of the crystal data.

The large error (4.2%) seen in Mol 115 is most likely due to experimental inaccuracy, since the observed bond length (1.44 Å) is unusually short (by ~ 0.05 Å) compared with any other bond length of this class of molecules (see 1.487 Å of Mol 114).

The errors in C-C(=O) bond lengths of esters and acids are in most cases within 1.5% of both the gas phase and crystal data (gas phase data are available only for acetic acid, Mol 33).

An error (3.2%) seen in Mol 73 is due to experimental inaccuracy (0.04 Å estimated deviation in bond length). An error (4.7%) in Mol 94 is also due to experimental inaccuracy, since the observed bond length (1.46 Å) is significantly shorter (by ~ 0.06 Å) than others of the same class of molecules.

The errors in the C-C=O bond angles of esters and acids are in most cases within 2.5% of the gas phase (1.3% on average for 2 molecules) and crystal data. The largest error (3.6%) seen in Mol 125 (δ lactone) is ascribed to the potential function, since the observed three bond angles about the carbonyl carbon are all nearly 120° , which is in accordance with the sp^2 hybridization and the planarity observed around the C(=O)-O-C group.

An error (3.5%) seen in Mol 34 is most likely due to experimental

inaccuracy, since the observed bond angle (129°) is considerably larger than that (126°) of a similar molecule (Mol 73) and the gas phase data of other molecules (e.g., 126.6° and 126.7° in Mols 33 and 93, respectively).

The errors (over $\sim 2\%$) in bond angles of Mols 82, 86, 88, 89 and 94 are accompanied by quite large errors (seen previously) in the corresponding C(=O)-O bond lengths of these molecules (i.e., 4.7, 5.1, 2.6, 5.1 and 4.0%, respectively).

The errors in the O-C=O bond angles of esters and acids are in most cases within 2.0% of both the gas phase (1.0% on average for 2 molecules) and crystal data. The largest error (3.2%) in the bond angle of Mol 94 is accompanied by a large error (4.0%) seen previously in the C(=O)-O bond length.

The errors in the C-C=O bond angles of aldehydes and ketones are within $\sim 1.0\%$ of the gas phase data (0.7% on average for 5 molecules) and in most cases within $\sim 1.5\%$ of the crystal data, and are comparable to those in the corresponding C-C(=O) and C=O bond lengths. The largest error (3.0%) in the C-C=O bond angle is seen in Mol 115, where the large error (4.2%) was also seen previously in the corresponding C-C(=O) bond length.

E. Amides:

The errors in the C-C(=O) bond length are within 2% of both the gas phase (0.3% on average for 2 molecules) and crystal data except those of Mols 59 (3.3%) and 83 (3.0%). The significantly short bond lengths 1.47 and 1.48 Å in Mols 59 and 83, respectively, compared with those (~ 1.50 Å) of all other molecules studies here are most likely

ascribed to experimental inaccuracies of the X-ray diffraction data.

The errors in the C-N(-C=O) bond lengths are within 2% of both the gas phase (0.6% on average for 2 molecules) and crystal data except an error (2.8%) seen in Mol 83 (132 atoms) which is most likely due to the accuracy limitation of the X-ray diffraction data.

The C(=O)-N bond lengths in the gas phase (e.g., 1.35 Å in Mol 46) are significantly longer than those in the crystal ($\sim$ 1.32 Å), and the large discrepancies seen between the calculated bond lengths and the crystal data should be attributed to the parameters of the potential function which are obtained from the gas phase data (average error in this bond length is 1.0% of the gas phase data for 3 molecules).

The shorter C-N bond length observed in the crystal is ascribed to the valence bond resonance form $\overset{+}{N}=C-\overset{-}{O}$ which can enhance the strength of the hydrogen bond N-H...O(=C) present in the crystal.

This double bond character of the C-N bond does not seem to be seen in Mols 58 and 66, since these two molecules are not capable of forming hydrogen bonds, and the observed C-N bond lengths in the crystal (1.37 and 1.35 Å in Mols 58 and 66, respectively) are comparable to those in the gas phase.

This resonance form is consistent with the observed C=O bond lengths (longer in the crystal), and with the observed N-C=O and C-C=O bond angles where these two bond angles in the crystal are close to 120°.

The considerably shorter C-N bond lengths found in Mol 46 (1.30 Å) and 49 (1.29 Å) are probably due to experimental inaccuracies of the X-ray diffraction data, where the estimated deviations in the bond lengths are 0.01 Å in both molecules.

The large errors of Mol 59 in the C=O bond length (4.5%), and the C-C=O (4.3%) and N-C=O (6.6%) bond angles can most likely be ascribed to the experimental errors, since the C=O bond length observed (1.28 Å) is longer than any other bond length observed in the crystal, and the deviations in the bond angles (9° and 6° in the C-C=O and N-C=O bond angles, respectively) from 120° are considerably larger compared with those in the other molecules.

The observed N-C=O bond angle (117.0°) of Mol 66 differs significantly from that (121.0°) of a structurally similar molecule (Mol 58), and this difference in bond angle may be due to the difference in the steric interaction of the phenyl group with the C=O group, since the phenyl groups are inclined from the amino plane by ~90° and ~60° in Mols 66 and 58, respectively. There is also a possibility that there exists a substantial difference in the crystal packing effect experienced by these molecules, which is not taken into account in our geometry calculation of a single molecule.

Energy:

Since, in our empirical potential function, the total energy (Eq. 1) of a molecule is not put on an absolute scale, application of it is restricted to evaluation of the relative energies in a series of related systems such as the energy difference between various conformers and intermolecular interaction energies. Relative energies are expected to be reliably determined, since intrinsic defects, if any, in the potential function would tend to cancel. This is observed in the good agreements obtained with experimental findings for the calculations

of rotational barrier heights (see Table 11), hydrogen bond energies (see Table 12), and lattice energies (see Table 8).

In Table 11 are given the results of calculations on the barrier heights of the internal rotation and conformational energy differences obtained by the adiabatically relaxed rotation. Although the results given in Table 11 were obtained by using all of the energy components in Eq. (1), the electrostatic interaction term (E^{el}) was found to have no appreciable effect on the evaluation of these relative energies.

In the study of internal rotation it was found that, to obtain reliable evaluations of the barrier height and energy differences between the conformers, complete relaxation of the molecular structure should be allowed during the energy minimization. Therefore, it is important for the potential function to include both intra- and intermolecular energy terms.

For example, butadiene has two stable conformers (i.e., cis and trans forms) in the internal rotation about a central single C-C bond, and it was found that both the observed barrier height and energy difference between these two conformers could not be reproduced without allowing distortion in the C-C bond length and adjacent C-C=C bond angles.

This flexibility will become more important in the conformational study of the molecule with large numbers of conformational degrees of freedom, since inclusion of the possible distortion of the geometry in the calculation would make more difference in the positions of local minima in the potential energy surface than in small molecules.

This is also important in the study of the intermolecular inter-

actions, since small changes in the conformation of the individual molecule could cause considerable effect on the intermolecular interaction, especially when the molecules are in close contact.

In Table 12 are given the results of the calculations of hydrogen bond energies, and the calculated hydrogen bond energy is defined as the total energy of the donor-acceptor complex at the energy minimum minus the total energy at infinite separation. The minimum energy structure of a hydrogen bond was found to be that in which the O-H group and the carbonyl O atom (i.e., acceptor atom) make a linear O-H...O bond, but the O-H axis was not aligned with the O=C axis (i.e., O-H axis aligned with an axis made of lone pair electron and nucleus of carbonyl oxygen). The functional form commonly used by other authors for the hydrogen bond potential is either (exp-6) or Lennard-Jones (6-12) type, and the same functional form as the non-bonded interaction potential is usually used (e.g., see 6-12 potential in Reference 1a).

In Table 7 are given the calculated lattice constants and crystal (i.e., binding) energies of the various molecular crystals together with the experimental values. Relatively large discrepancies in lattice constant β between the calculated and observed experimental values are found in molecules (see Fig. 3) 15 ($\Delta\beta=-8.3$) and 16 ($\Delta\beta=-5.2$), since in these molecular crystals there exists the hydrogen bonding which was not taken into account in our crystal packing calculations (i.e., only the non-bonded and electrostatic interactions were used).

Although a direct comparison of this study with those of other authors is difficult because of differing functional forms used and molecules studied, we can comment to some extent on the accuracy of our

potential function relative to those of other authors. For this purpose, two different studies done by other authors will be appropriate to cite here, each of which focused on intra- and intermolecular interaction, respectively.

The extensive calculations on mono- and polycyclic saturated hydrocarbons were done by two groups, Allinger's^{2a} and Schleyer's^{2b} groups, and the agreements of their results with the observed bond lengths and angles of the gas phase data are excellent (within 1% of the experimental findings in most cases). Although our results on all the gas phase structures studied here are slightly inferior to their results, the agreements of our results with the observed bond lengths and angles are still comparable to their results in most cases (within ~1% and ~2% for bond lengths and angles, respectively). Allowing for the complexity in chemical compositions and structures of the molecules studied here compared with molecules (i.e., molecules composed of only C and H atoms and a single bond) studied by them, our results should be regarded as quite satisfactory.

Scheraga's group^{1a} has done extensive studies on the crystal structures of amides and other molecules, and has calculated the lattice constants and lattice binding energies in the same way as we have done in our crystal packing calculations. The agreements of their calculation with experimental values are comparable to those of our results presented in Table 8. A functional form used by these authors for non-bonded interaction energies is a Lennard-Jones (6-12) potential and has only two parameters (i.e., coefficients of the attractive and repulsive parts). On the other hand, in our potential the (exp-6) form

was used which has three parameters (see Eq. 8) and, due to this additional parameter, our results were expected to give better agreements than theirs. However, in their potential function, different values of parameters were used, depending on the types of atoms (e.g., aliphatic C, aromatic C, etc.), while in our case the same value of parameter was used for the same atom (e.g., same parameter for all types of C atoms).

The accuracy of the predicted geometric parameters by our potential function is ~ 0.01 Å for bond lengths and $\sim 2^\circ$ for bond angles, $\sim 3^\circ$ for torsional angles and ~ 0.05 Å for non-bonded distances. As we have seen, the calculated molecular structures gave better agreements with the gas phase data than with the crystal data. However, in order to compare the calculated molecular structures of the crystal with the observed ones, further calculations will have to be pursued, where a number of molecules are included to simulate the effect due to the intermolecular interactions, since in our geometry calculation only a single molecule was used.

Our potential function includes both intra- and intermolecular interactions over a broad range of molecules, and will provide a powerful tool, especially for large molecular systems where neither the quantum mechanical method nor the direct experimental information is available.

Further studies for the ionic molecules are needed, which would concern the choice of the charge distribution and its effect on the calculated molecular structure, since in our study of zwitterions, for example, only a formal charge (e.g., +1 for quaternary nitrogen atom)

was used. Associated with this is a need for the additional development of the various types of hydrogen bond potentials (e.g., N-H..O), in order to study other biologically important systems.

Table 1. Designation of atom types

Atom(type)	Designation	Atom(type)	Designation
C(1)	Primary(SP^3)	N(1)	Primary amine(SP^3)
C(2)	Secondary(SP^3)	N(2)	Secondary amine(SP^3)
C(3)	Tertiary(SP^3)	N(3)	Tertiary amine(SP^3)
C(4)	Quaternary(SP^4)	N(4)	Quaternary(SP^4)
C(5)	Triple bond(SP)	N(5)	Aromatic(SP^2)
C(6)	Aromatic(SP^2)	N(8)	Amide(SP^2)
C(7)	Amide(SP^2)	N(9)	Double bond(SP^2)
C(8)	Carboxyl(SP^2)	N(10)	Triple bond(SP)
C(9)	Carbonyl(SP^2)	N(12)	Nitroso(SP^2)
C(10)	Double bond(SP^2)	N(13)	Nitro(SP^2)
C(13)	Carboxyl ion(SP^2)	N(X)	Any kind
C(X)	Any kind		

Table 2. Parameters determined for bond deformation energy^a

Bond	$r_{ij}^{(0)}$	f_{ij}^b	Bond	$r_{ij}^{(0)}$	f_{ij}^b
C(X)-C(X)	1.520	4.4	C(9)-C(10)	1.460	5.08
C(3)-C(4)	1.525	4.4	C(10)=C(10)	1.335	9.7
C(1)-C(10)	1.498	5.08	C(6)=C(6)	1.385	7.83
C(2)-C(10)	1.498	5.08	C(5)≡C(5)	1.207	15.6
C(3)-C(10)	1.498	5.08	C(X)-N(X)	1.460	4.6
C(4)-C(10)	1.500	5.08	C(6)-N(2)	1.386	4.6
C(1)-C(6)	1.510	5.08	C(10)-N(2)	1.330	4.6
C(2)-C(6)	1.510	5.08	C(1)-N(4)	1.495	4.6
C(3)-C(6)	1.510	5.08	C(2)-N(4)	1.495	4.6
C(4)-C(6)	1.508	5.08	C(3)-N(4)	1.495	4.6
C(1)-C(5)	1.465	5.3	C(4)-N(4)	1.495	4.6
C(2)-C(5)	1.465	5.3	C(6)=N(5)	1.360	10.0
C(3)-C(5)	1.465	5.3	C(1)-N(8)	1.460	5.0
C(4)-C(5)	1.465	5.3	C(2)-N(8)	1.460	5.0
C(1)-C(9)	1.501	4.8	C(3)-N(8)	1.460	5.0
C(2)-C(9)	1.501	4.8	C(6)-N(8)	1.410	5.0
C(3)-C(9)	1.501	4.8	C(7)-N(8)	1.350	7.5
C(4)-C(9)	1.501	4.8	C(10)=N(9)	1.320	10.0
C(6)-C(9)	1.495	5.08	C(6)-N(9)	1.370	4.6
C(1)-C(8)	1.495	5.08	C(5)≡N(10)	1.154	18.1
C(2)-C(8)	1.495	5.08	C(1)-N(12)	1.480	4.6
C(3)-C(8)	1.500	5.08	C(1)-N(13)	1.470	4.6
C(4)-C(8)	1.500	5.08	C(6)-N(13)	1.470	4.6
C(1)-C(7)	1.500	5.0	C(1)-O	1.425	5.0
C(2)-C(7)	1.500	5.0	C(2)-O	1.425	5.0
C(3)-C(7)	1.500	5.0	C(3)-O	1.425	5.0
C(4)-C(7)	1.500	5.0	C(4)-O	1.425	5.0
C(6)-C(7)	1.510	5.0	C(6)-O	1.370	5.0
C(6)-C(6)	1.469	5.08	C(10)-O	1.344	5.0
C(10)-C(10)	1.460	5.08	C(8)-O	1.340	5.0
C(6)-C(10)	1.455	5.08	C(8)=O	1.221	12.0

Table 2. (continued)^a

Bond	$r_{ij}^{(0)}$	f_{ij}^b	Bond	$r_{ij}^{(0)}$	f_{ij}^b
C(9)=O	1.221	11.0	H-C(6)	1.085	5.0
C(7)=O	1.220	10.0	H-C(5)	1.057	5.85
C(13)-O	1.440	5.08	H-C(10)	1.085	5.1
N(12)=O	1.220	9.13	H-N(X)	1.016	6.4
N(13)-O	1.220	9.13	H-N(4)	1.039	6.4
H=C(X)	1.095	4.6	H-O	0.958	7.0

^a $r_{ij}^{(0)}$ and f_{ij}^b are in units of angstrom and mdyne/Å, respectively. See Table 1 for the description of bond types.

Table 3. Parameters determined for angle deformation energy^a

Angle	$\theta_{ijk}^{(0)}$	f_{ijk}^{θ}	Angle	$\theta_{ijk}^{(0)}$	f_{ijk}^{θ}
C(X)-C(2)-C(X)	110.4	0.57	C(3)-C(7)-N(8)	114.6	0.98
C(X)-C(3)-C(X)	110.1	0.57	C(4)-C(7)-N(8)	114.6	0.98
C(X)-C(4)-C(X)	109.5	0.57	C(6)-C(7)-N(8)	114.6	0.98
C(1)-C(9)-C(1)	117.2	1.1	C(1)-C(6)-N(2)	116.0	0.55
C(2)-C(9)-C(2)	117.2	1.1	C(6)-C(6)-N(2)	116.0	0.55
C(3)-C(9)-C(3)	117.2	1.1	C(6)=C(6)-N(2)	120.0	0.55
C(4)-C(9)-C(4)	117.2	1.1	C(6)=C(6)-N(13)	120.0	0.55
C(1)-C(9)-C(6)	120.0	1.1	C(6)=C(6)-N(8)	120.0	0.55
C(6)-C(9)-C(6)	120.0	1.1	C(6)=C(6)-N(9)	120.0	0.55
C(10)-C(9)-C(10)	117.2	1.1	C(10)-C(6)=N(5)	120.0	0.55
C(X)-C(10)-C(X)	114.0	1.1	C(6)=C(6)=N(5)	120.0	0.55
C(6)-C(6)-C(9)	120.0	0.55	C(X)-C(X)-O	108.5	0.98
C(1)-C(6)=C(6)	120.0	0.55	C(X)-C(3)-O	109.5	0.98
C(2)-C(6)=C(6)	120.0	0.55	C(2)-C(10)-O	108.5	0.98
C(3)-C(6)=C(6)	120.0	0.55	C(X)-C(8)-O	112.0	0.98
C(4)-C(6)=C(6)	120.0	0.55	C(6)=C(6)-O	120.0	0.65
C(10)-C(6)=C(6)	120.0	0.55	C(10)=C(10)-O	117.0	1.1
C(9)-C(6)=C(6)	120.0	0.55	C(1)-C(9)=O	122.0	0.65
C(7)-C(6)=C(6)	120.0	0.55	C(2)-C(9)=O	122.0	0.65
C(X)-C(10)=C(10)	121.5	1.1	C(3)-C(9)=O	122.0	0.65
C(6)=C(6)=C(6)	120.0	0.55	C(4)-C(9)=O	122.0	0.65
C(X)-C(2)-N(X)	111.0	0.57	C(6)-C(9)=O	120.0	0.65
C(X)-C(3)-N(X)	110.7	0.57	C(10)-C(9)=O	122.0	0.65
C(X)-C(4)-N(X)	109.5	0.57	C(X)-C(8)=O	125.7	0.98
C(2)-C(2)-N(4)	105.2	0.57	C(1)-C(7)=O	123.5	0.98
C(3)-C(2)-N(4)	105.2	0.57	C(2)-C(7)=O	123.5	0.98
C(1)-C(3)-N(4)	105.2	0.57	C(3)-C(7)=O	123.5	0.98
C(3)-C(3)-N(4)	105.2	0.57	C(4)-C(7)=O	123.5	0.98
C(1)-C(7)-N(8)	114.6	0.98	C(6)-C(7)=O	123.5	0.98
C(2)-C(7)-N(8)	114.6	0.98	C(2)-C(13)=O	117.0	0.98

Table 3. (continued)^a

Angle	$\theta_{ijk}^{(0)}$	f_{ijk}^{θ}	Angle	$\theta_{ijk}^{(0)}$	f_{ijk}^{θ}
C(3)-C(13)=O	117.0	0.98	C(1)-N(8)-C(6)	120.0	0.8
N(8)-C(7)=O	123.6	0.98	C(6)-N(8)-C(6)	120.0	0.8
N(2)-C(10)=N(9)	113.2	1.1	C(6)-N(9)=C(10)	105.4	1.0
N(9)-C(6)=N(5)	120.0	0.55	C(6)=N(5)=C(6)	109.7	0.55
N(5)=C(6)=N(5)	128.1	0.55	C(1)-N(12)=O	110.0	0.98
O-C(3)-O	109.5	0.57	C(1)-N(13)=O	117.4	0.65
O-C(9)=O	122.3	0.98	C(6)-N(13)=O	117.4	0.65
O=C(13)=O	126.0	0.98	O=N(13)=O	125.3	1.52
C(X)-N(X)-C(X)	109.0	1.1	C(X)-O-C(X)	110.0	0.6
C(6)-N(2)-C(6)	112.0	1.3	C(3)-O-C(3)	108.0	1.0
C(6)-N(2)-C(10)	111.0	1.1	C(3)-O-C(4)	108.0	1.0
C(1)-N(8)-C(7)	117.5	0.8	C(6)-O-C(6)	114.2	1.3
C(2)-N(8)-C(7)	119.0	0.8	C(1)-O-C(8)	107.0	0.6
C(3)-N(8)-C(7)	117.5	0.8	C(2)-O-C(8)	107.0	0.6
C(6)-N(8)-C(7)	120.0	0.8	C(3)-O-C(8)	107.0	0.6
H-C(1)-H	109.2	0.33	H-C(8)-N(8)	112.7	0.98
H-C(2)-H	109.1	0.33	H-C(5)=N(10)	180.0	0.24
H-C(9)-H	116.5	1.1	H-C(6)-N(2)	116.0	0.55
H-C(10)-H	118.0	0.65	H-C(10)=N(9)	138.2	0.65
H-C(1)-C(X)	109.5	0.40	H-C(6)=N(5)	120.0	0.55
H-C(2)-C(X)	109.0	0.40	H-C(10)-N(2)	108.6	1.1
H-C(3)-C(X)	109.2	0.40	H-C(9)=O	121.7	0.65
H-C(10)-C(1)	117.5	1.1	H-C(X)-O	109.5	0.50
H-C(10)-C(10)	116.5	1.1	H-C(8)-O	109.5	0.50
H-C(10)-C(X)	119.0	0.65	H-C(8)=O	124.8	0.65
H-C(6)=C(6)	120.0	0.55	H-C(7)=O	122.4	0.98
H-C(10)=C(10)	121.0	0.65	H-C(6)-O	106.0	0.55
H-C(5)=C(5)	180.0	0.24	H-N(X)-H	110.0	0.8
H-C(1)-N(X)	109.5	0.40	H-N(8)-H	120.0	0.8
H-C(2)-N(X)	109.0	0.40	H-N(X)-C(X)	111.0	0.8
H-C(3)-N(X)	109.2	0.40	H-N(2)-C(10)	125.0	0.8

Table 3. (continued)^a

Angle	$\theta_{ijk}^{(0)}$	f_{ijk}^{θ}	Angle	$\theta_{ijk}^{(0)}$	f_{ijk}^{θ}
H-N(2)-C(6)	124.0	1.3	H-O-H	105.0	0.69
H-N(8)-C(1)	120.0	0.8	H-O-C(X)	108.0	0.76
H-N(8)-C(2)	120.0	0.8	H-O-C(8)	103.3	0.76
H-N(8)-C(6)	120.0	0.8	H-O-O	93.2	0.5
H-N(8)-C(7)	120.0	0.8			

^a $\theta_{ijk}^{(0)}$ and f_{ijk}^{θ} are in units of degree and mdyne Å/rad², respectively. See Table 1 for the description of angle types.

Table 4. Parameters determined for torsional strain energy

$\phi(i-j-k-l)^a$	func.	$U_{ijkl}^c(U'_{ijkl})$	$\phi(i-j-k-l)^a$	func.	$U_{ijkl}^c(U'_{ijkl})$
H-C(X)-C(X)-H	1	0.1164	H-C(6)=C(6)-N(X)	4	2.0
H-C(1)-C(9)-H	1	0.10	H-C(3)-C(6)=N(5)	1	0.1
H-C(1)-C(10)-H	1	0.25	H-C(1)-C(5)=N(10)	1	0.0
H-C(2)-C(10)-H	1	0.20	H-C(2)-C(5)=N(10)	1	0.0
H-C(3)-C(10)-H	1	0.20	H-C(1)-C(8)=O	1	-0.02
H-C(6)=C(6)-H	4	2.0	H-C(2)-C(8)=O	1	-0.03
H-C(10)=C(10)-H	4	7.5	H-C(3)-C(8)=O	1	-0.03
H-C(10)-C(10)-H	4	0.10	H-C(1)-C(8)-O	1	0.02
H-C(9)-C(10)-H	4	0.10	H-C(2)-C(8)-O	1	0.10
H-C(5)=C(5)-H	1	0.0	H-C(3)-C(8)-O	1	0.10
H-C(X)-C(X)-C(X)	1	0.1164	H-C(1)-C(9)=O	1	-0.10
H-C(X)-C(6)=C(6)	1	0.10	H-C(2)-C(9)=O	1	-0.10
H-C(6)=C(6)-C(X)	4	2.0	H-C(3)-C(9)=O	1	-0.10
H-C(6)=C(6)=C(6)	4	2.0	H-C(10)-C(9)=O	4	0.10
H-C(2)-C(9)-C(X)	1	0.03	H-C(X)-C(X)-O	1	0.165
H-C(3)-C(9)-C(X)	1	0.03	H-C(2)-C(13)=O	1	-0.03
H-C(1)-C(9)-C(X)	1	0.03	H-C(3)-C(13)=O	1	-0.03
H-C(10)=C(10)-C(X)	4	7.5	H-C(10)=C(10)-O	4	7.5
H-C(10)-C(2)-C(X)	1	0.25	H-C(6)=C(6)-O	4	2.0
H-C(10)=C(3)=C(X)	1	0.25	H-C(1)-C(7)=O	1	0.5
H-C(10)=C(4)=C(X)	1	0.25	H-C(2)-C(7)=O	1	-0.5
H-C(1)-C(10)-C(X)	1	0.25	H-C(3)-C(7)=O	1	0.5
H-C(2)-C(10)-C(X)	1	0.25	C(X)-C(X)-C(X)-C(X)	1	0.07464
H-C(3)-C(10)-C(X)	1	0.25	C(X)-C(X)-C(6)=C(6)	1	0.1
H-C(10)-C(10)-C(X)	4	0.10	C(X)-C(6)=C(6)=C(6)	4	2.0
H-C(X)-C(10)=C(10)	1	-0.2	C(X)-C(6)=C(6)-C(X)	4	2.0
H-C(1)-C(10)=C(10)	1	-0.2	C(6)=C(6)=C(6)=C(6)	4	5.0
H-C(9)-C(10)=C(10)	4	0.10	C(6)=C(6)-C(9)-C(X)	4	0.4
H-C(10)-C(10)=C(10)	4	0.10	C(X)-C(2)-C(9)-C(X)	1	0.03
H-C(9)-C(10)-C(X)	4	0.10	C(X)-C(3)-C(9)-C(X)	1	0.03
H-C(1)=C(3)=C(5)	1	0.0	C(X)=C(4)=C(9)-C(X)	1	0.03
H-C(3)=C(5)=C(5)	1	0.0	C(X)-C(10)=C(10)-C(X)	4	7.5
H-C(5)=C(5)-C(X)	1	0.0	C(X)-C(2)-C(10)-C(X)	1	0.165
H-C(X)-C(X)-N(X)	1	0.12	C(X)-C(3)-C(10)-C(X)	1	0.165
H-C(6)=C(6)=N(5)	4	2.0	C(X)-C(X)-C(10)=C(10)	1	-0.2

Table 4. (continued)

$\phi(i-j-k-l)^a$	func.	$U_{ijkl}^c(U'_{ijkl})$	$\phi(i-j-k-l)^a$	func.	$U_{ijkl}^c(U'_{ijkl})$
$C(6)=C(6)-C(10)=C(10)$	5	2.4(-0.53)	$C(X)-C(10)=C(10)-O$	4	7.5
$C(10)=C(10)-C(10)=C(10)$	5	2.4(-0.15)	$C(6)=C(6)=C(6)-O$	4	2.0
$C(6)=C(6)-C(6)=C(6)$	4	1.0	$C(6)=C(6)-C(7)=O$	4	0.4
$C(X)-C(5)=C(5)-C(X)$	1	0.0	$C(X)-C(3)-C(13)=O$	1	-0.03
$C(X)-C(3)-C(5)=C(5)$	1	0.0	$C(X)-C(2)-C(7)=O$	1	-0.5
$C(X)-C(4)-C(5)=C(5)$	1	0.0	$C(X)-C(3)-C(7)=O$	1	0.5
$C(X)-C(X)-C(X)-N(X)$	1	0.08	$C(X)-C(4)-C(7)=O$	1	0.5
$C(10)=C(10)-C(X)-N(X)$	1	0.08	$C(X)-C(6)=C(6)-O$	4	2.0
$C(6)=C(6)-C(X)-N(X)$	1	0.08	$C(6)-C(6)-C(9)=O$	4	0.4
$C(X)-C(6)=C(6)=N(5)$	4	2.0	$N(X)-C(6)=C(6)-N(X)$	4	2.0
$C(6)=C(6)=C(6)=N(5)$	4	5.0	$N(X)-C(6)=C(6)=N(5)$	4	2.0
$C(X)-C(6)=C(6)-N(X)$	4	2.0	$N(X)-C(X)-C(X)-O$	1	0.11
$C(6)=C(6)=C(6)-N(X)$	4	2.0	$N(X)-C(2)-C(13)=O$	1	-0.03
$C(6)=C(6)-C(7)-N(3)$	4	4.0	$N(X)-C(3)-C(13)=O$	1	-0.03
$C(X)-C(10)-C(6)=N(5)$	4	0.4	$O-C(2)-C(8)=O$	1	-0.03
$C(X)-C(3)-C(6)=N(5)$	1	0.1	$O-C(3)-C(8)=O$	1	-0.03
$C(6)=C(6)-C(6)=N(5)$	4	0.2	$O-C(4)-C(8)=O$	1	-0.03
$C(X)-C(6)-C(6)=N(5)$	4	0.2	$O-C(3)-C(9)=O$	1	-0.1
$C(X)-C(2)-C(5)=N(10)$	1	0.0	$O-C(X)-C(X)-O$	1	0.11
$C(X)-C(4)-C(5)=N(10)$	1	0.0	$O-C(6)=C(6)-O$	4	2.0
$C(X)-C(X)-C(X)-O$	1	0.11	$H-C(X)-N(X)-H$	1	0.12
$C(X)-C(2)-C(8)=O$	1	-0.03	$H-C(7)-N(8)-H$	4	0.1
$C(X)-C(3)-C(8)=O$	1	-0.03	$H-C(X)-N(X)-C(X)$	1	0.4
$C(X)-C(4)-C(8)=O$	1	-0.03	$H-C(6)-N(5)-C(6)$	4	2.0
$C(X)-C(2)-C(8)-O$	1	0.1	$H-C(10)=N(9)-C(X)$	4	7.5
$C(X)-C(3)-C(8)-O$	1	0.1	$H-C(6)-N(9)=C(10)$	1	0.5
$C(X)-C(4)-C(8)-O$	1	0.1	$H-C(1)-N(13)=O$	1	0.0
$C(6)=C(6)-C(9)=O$	4	0.4	$H-C(1)-N(12)=O$	1	-0.18
$C(X)-C(2)-C(9)=O$	1	-0.1	$C(X)-C(X)-N(2)-H$	1	0.12
$C(X)-C(3)-C(9)=O$	1	-0.1	$C(6)=C(6)-N(2)-H$	4	2.0
$C(X)-C(4)-C(9)=O$	1	-0.1	$C(X)-C(X)-N(X)-C(X)$	1	0.08
$C(X)-C(10)-C(9)=O$	4	0.1	$C(6)=C(6)-N(2)-C(X)$	4	2.0
$C(10)=C(10)-C(X)-O$	3	0.0(0.1)	$C(6)=C(6)=N(5)=C(6)$	4	5.0
$C(10)=C(10)-C(9)=O$	5	3.4(-0.37)	$C(X)-C(7)-N(8)-C(X)$	4	0.1

Table 4. (continued)

$\phi(i-j-k-1)^a$	func.	$U_{ijkl}^c(U'_{ijkl})$	$\phi(i-j-k-1)^a$	func.	$U_{ijkl}^c(U'_{ijkl})$
C(6)=C(6)-N(9)=C(10)	4	1.0	H-C(10)-O-C(X)	1	0.11
C(6)=C(6)=N(13)=O	1	0.9	H-C(6)-O-C(6)	4	2.0
C(X)-C(7)=N(8)=H	4	0.1	C(X)-C(2)-O-C(X)	1	0.20
N(9)=C(10)=N(2)=H	1	0.12	C(X)-C(3)-O-C(X)	1	0.20
N(9)=C(10)-N(2)-C(X)	1	0.08	C(X)-C(4)-O-C(X)	1	0.20
N(X)-C(10)=N(9)-C(X)	4	7.5	C(10)-C(8)-O-C(X)	4	3.0
N(5)=C(6)=N(5)=C(6)	4	5.0	C(10)=C(10)-O-C(X)	4	-2.0
N(X)-C(6)=N(5)=C(6)	4	2.0	C(X)-C(6)-O-C(X)	4	2.0
N(5)=C(6)-N(9)=C(10)	4	0.1	C(X)-C(8)-O-H	4	0.165
O=C(7)-N(8)-H	4	4.5	C(X)-C(X)-O-H	1	0.165
O=C(7)-N(8)-C(X)	4	4.5	C(6)=C(6)-O-H	4	1.1
H-C(8)-O-H	4	0.11	C(6)=C(6)-O-C	4	1.0
H-C(X)-O-H	1	0.11	O=C(8)-O-H	5	4.95(1.05)
H-C(1)-O-C(X)	1	0.20	O-C(3)-O-H	1	0.165
H-C(2)-O-C(X)	1	0.20	O=C(8)-O-C(X)	5	3.0(1.0)
H-C(3)-O-C(X)	1	0.20	O-C(3)-O-C(X)	1	0.2
H-C(8)-O-C(X)	5	2.0(-1.0)	O-C(4)-O-C(X)	1	0.2

^a See Table 1 for the description of the dihedral angles.

^b func. 1,4,5 refer to $U_{ijkl}(1+\cos 3\phi)$, $U_{ijkl}(1-\cos 2\phi)$ and $U_{ijkl}(1-\cos 2\phi)+U_{ijkl}(1-\cos \phi)$, respectively.

^c Unit is in kcal/mol.

Table 5. Bond moments

Bond ^a	Bond moment (Debye) ^d	Bond ^a	Bond moment (Debye) ^d
C-H	0.4	N-H	1.31
N-C	0.22	O-H	1.51
N=C	0.9	C-C	0.0
O-C	0.74	C=C	0.0(0.767 ^b , 0.249 ^c)
O=C	2.3		

^a The first atom of each pair is the negative end of the bond moment.

^b if attached to C-N bond. ^c if attached to C-O bond. ^d Data from ref.

8.

Table 6. Calculation of the dipole moment(Debye)

Molecule	$\mu_{\text{calcd}}^{\text{h}}$	$\mu_{\text{exptl}}^{\text{a}}$	$\mu_{\text{qc}}^{\text{i}}$	Molecule	$\mu_{\text{calcd}}^{\text{h}}$	$\mu_{\text{exptl}}^{\text{a}}$	$\mu_{\text{qc}}^{\text{i}}$
H ₂ O	1.83	1.85	1.78 ^c	CH ₃ COOH	1.23	1.75	
			2.68 ^d	C ₂ H ₅ COOH	1.26	1.76	
CH ₃ OH	1.56	1.69	1.51 ^c	HCOOCH ₃	1.63	1.77	
			2.43 ^d	CH ₃ COOCH ₃	1.67	1.71	
C ₂ H ₅ OH	1.56	1.71		CH ₃ COOC ₂ H ₅	1.63	1.78	
CH ₃ OCH ₃	1.25	1.30		Pyrrole	2.17	1.5-2.2	2.01 ^e
CH ₂ O	2.74	2.34	1.53 ^c			1.74	
			3.11 ^d	Carbazole	1.80	2.2 ^b	1.66 ^f
CH ₃ CHO	2.79	2.68	1.66 ^c			1.7 ^b	2.21 ^g
(CH ₃) ₂ CO	2.77	2.90	1.87 ^c			1.9 ^b	
CH ₂ CHCHO	2.73	3.04	4.09 ^d	Furan	0.73	0.67	0.62 ^e
HCOOH	1.26	1.35	0.97 ^c				
			1.49 ^d				

^a Data from ref 144a unless otherwise noted. ^b Reference 144b. ^c Reference 9a. ^d Reference 9b. ^e Reference 144e. ^f Reference 144f. ^g Reference 144g. ^h Calculation by this work. ⁱ ab initio SCF calculation.

Table 7. Parameters for nonbonded interaction energy

Atom pair	a_{ij} (kcal/mol)	b_{ij} ($\text{\AA}^{-1}$)	c_{ij} (kcal $\text{\AA}^6$ /mol)
H...H	6515.4	3.75	85.97
H...C	4874.8	3.582	84.7
H...N	20300.0	3.63	255.0
H...O	20300.0	3.65	255.0
C...C	15465.9	3.117	618.9
C...N	31274.0	3.31	685.5
C...O	31274.0	3.34	685.5
N...N	63240.0	3.50	760.0
N...O	63240.0	3.53	760.0
O...O	63240.0	3.55	760.0

Table 8. Crystal packing calculation

Mole- cule	Space group	Cell ^a index	a ^h , Å	b ^h , Å	c ^h , Å	α^h , deg	β^h , deg	γ^h , deg	E _{cr} ^{exptl} kcal/mol	Δa^g , Å	Δb^g , Å	Δc^g , Å	$\Delta \alpha^g$, deg	$\Delta \beta^g$, deg	$\Delta \gamma^g$, deg	E _{cr} ^{calcd} kcal/mol	Ref. ^b
1	Pbcn	753	4.10	9.04	14.70	90.0	90.0	90.0	-10.0 ^c	0.31	-0.02	0.16				-10.8	5b
2	P1	575	4.17	4.70	8.57	96.6	87.2	105.0	-12.2 ^c	0.30	-0.10	0.11	0.5	0.9	-1.8	-12.8	6
3	P1	573	4.22	4.79	11.02	94.7	84.3	105.8	-16.3 ^c	0.21	-0.17	0.07	0.3	0.8	-3.0	-16.8	146a
4	C2/c	355	11.23	6.44	8.20	90.0	108.3	90.0		0.15	0.05	0.40		-0.1		-11.6	8c
5	P2 ₁ /n	757	4.63	6.62	4.07	90.0	94.4	90.0		-0.22	0.13	-0.02		-2.3		-5.0	94f
6	Pbca	555	7.39	9.42	6.81	90.0	90.0	90.0	-11.3 ^d	-0.01	0.17	-0.19				-11.0	100a
7	P2 ₁ /a	553	8.33	6.00	8.66	90.0	122.0	90.0		-0.38	-0.32	0.19		-0.7		-18.2	101a
8	P2 ₁ /a	553	8.56	6.04	11.16	90.0	124.7	90.0	-22.6 ^e	-0.26	-0.29	0.16		0.0		-25.3	102b
									-24.5 ^c								
9	Pnma	535	7.77	19.18	5.73	90.0	90.0	90.0	-21.9 ^f	-0.12	-0.01	-0.16				-25.7	81b
10	P2 ₁ /c	555	10.27	12.09	12.36	90.0	102.2	90.0		0.01	-0.09	-0.01		-1.7		-40.8	90
11	P2 ₁	535	8.04	28.53	7.32	90.0	111.0	90.0		0.09	0.53	0.00		0.5		-60.2	129
12	P2 ₁ /n	573	7.64	4.14	13.45	90.0	90.4	90.0		0.12	0.01	-0.32		-1.3		-25.8	146b
13	P2 ₁ /a	533	6.20	12.14	12.86	90.0	86.4	90.0		0.24	-0.03	0.00		1.0		-25.4	146c
14	P2 ₁ /c	575	14.92	4.09	16.68	90.0	109.7	90.0		0.01	-0.05	0.49		-0.2		-24.7	39
15	P2 ₁ /n	557	10.01	12.93	7.41	90.0	91.5	90.0		0.20	0.73	0.07		-8.3		-23.5	40
16	P2 ₁ /a	557	6.76	6.74	5.71	90.0	99.6	90.0		0.06	0.47	0.09		-5.2		-14.8	146d
17	P2 ₁ 2 ₁ 2	555	6.31	5.80	6.89	90.0	90.0	90.0		0.86	-0.38	0.24				-35.5	146e
18	P1	357	23.46	11.38	5.97	93.3	94.2	93.8		0.27	0.28	0.02	-1.5	-0.2	-0.6	-64.8	146f

^a The cell index shows the number of unit cells taken (including the unit cell containing the 0th molecule) along the unit cell axis, a, b, and c, respectively. ^b References of the X-ray data. ^c Reference 145a. ^d Reference 11. ^e Reference 145b. ^f Reference 145c. ^g The Δ 's are defined as $\Delta l = l_{\text{calcd}} - l_{\text{exptl}}$, where $l = a, b, c, \alpha, \beta$, and γ . ^h Experimental values.

Table 9. Calculated bond lengths

Bond ^a	Mole- cule ^b	r ^c calcd	r ^c exptl	Method ^d	Percent rel. error ^e	Ref. ^f	Bond ^a	Mole- cule ^b	r ^c calcd	r ^c exptl	Method ^d	Percent rel. error ^e	Ref. ^f
C(X)-C(X)	1	1.529	1.543	Ir/Ra	-0.9	148a	C(3)-C(4)	126	1.546	1.523	Nd	1.5	142
			1.536	Ir	-0.5	148b		127	1.544	1.524	Nd	0.5	100b
			1.534	Ed	-0.3	148c		128	1.531	1.539	Nd	-0.5	14
			1.532	Ed	-0.2	148d		129	1.538 ^a	1.534	Nd	0.3	15
	2	1.530	1.526	Mw	0.3	149a			1.542 ^b	1.537		0.3	
			1.534	Mw/Ed	-0.3	149b		139	1.525	1.514	Ra	0.7	16a
	3	1.531	1.533	Ed	-0.1	150a				1.510	Ed	1.0	16b
			1.539	Ed	-0.5	150b		131	1.550	1.559	Xr	-0.6	17
	4	1.532	1.525	Mw	0.5	151a		132	1.559	1.558	Xr	0.1	18
			1.535	Mw/Ed	-0.2	151b		133	1.543	1.531	Xr	0.8	19
	5	1.532	1.531	Ed	0.1	154a		70	1.596	1.611	Ed	-0.9	144d
			1.525	Xr	0.5	154b		127	1.551	1.540	Nd	0.7	100b
	6	1.531	1.533	Ed	-0.1	154a	C(1)-C(10)	15	1.504	1.501	Mw	0.2	20a
			1.530	Xr	0.1	155				1.506	Ed	-0.1	20b
			1.548	Ed	-1.4	152a		16	1.505	1.507	Mw	-0.1	21a
	7	1.527	1.568	Ed	-2.6	152b				1.508	Ed	-0.2	21b
			1.558	Ra	-2.0	152c		17a	1.502	1.508	Ed	-0.4	22
			1.528	Ed	0.4	143a		17b	1.508	1.506	Ed	0.1	22
			1.528	Ed	0.4	143b		71a	1.506	1.515	Ed	-0.6	23
	8	1.534	1.528	Ed	0.4	143b		71b	1.507	1.515	Ed	-0.5	23
			1.526	Xr	0.5	143c		87	1.507	1.436	Xr	4.9	24
			1.546	Ed	-1.1	144c		24	1.508	1.510	Ed	-0.1	25
	9	1.529	1.539	Ed	-0.6	152a		25	1.508	1.511	Ed	-0.2	26
			1.539	Ed	-0.3	153a	C(2)-C(10)	22a	1.511	1.507	Ed	0.3	27
	69	1.534	1.540	Ed	-0.4	153b		22b	1.505	1.493	Ed	0.8	27
			1.548	Ed	-0.2	144d							

Table 9. (continued)

Bond ^a	Mole- cule ^b	r ^c _{calcd}	r ^c _{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f	Bond ^a	Mole- cule ^b	r ^c _{calcd}	r ^c _{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f
	71a	1.512	1.515	Ed	-0.2	23		79	1.544	1.570	Xr	-1.0	33
	71b	1.510	1.502	Ed	0.5	23		84	1.537	1.550	Xr	-0.8	46
	19	1.511	1.509	Mw	0.1	28	C(1)-C(5)	41	1.465	1.460	Mw	0.3	47a
	100	1.505	1.496	Ed	0.6	29				1.458	Mw	0.5	47b
C(3)-C(10)	80	1.508	1.516	Xr	-0.5	30		42	1.465	1.468	Ed	-0.2	48
	81	1.508	1.501	Xr	0.5	31		44	1.466	1.458	Mw	0.5	49a
	85	1.509	1.48	Xr	2.0	32				1.468	Ed	-0.1	49b
	87	1.524	1.519	Xr	0.3	24	C(2)-C(5)	45	1.468	1.474	Mw	-0.4	50a
C(4)-C(10)	79	1.517	1.512	Xr	0.3	33				1.459	Mw	0.6	50b
C(1)-C(5)	50	1.516	1.51	Ed	0.4	34	C(3)-C(5)	103	1.467	1.495	Mw	-1.9	51
	57	1.522	1.506	Xr	1.1	35	C(4)-C(5)	104	1.469	1.495	Mw	-1.7	52a
	75	1.524	1.526	Xr	-0.1	36				1.498	Ed	-1.9	52b
	92	1.519	1.521	Xr	-0.1	37		105	1.469	1.495	Mw	-1.7	52a
	98	1.519	1.509	Mw	0.7	38	C(1)-C(9)	27	1.510	1.501	Mw	0.6	53a
	114	1.516	1.494	Xr	1.5	39				1.512	Mw/Ed	-0.1	53b
	115	1.516	1.51	Xr	0.4	40		28	1.510	1.507	Mw	0.2	54a
	118	1.522	1.511	Xr	0.7	41				1.517	Mw/Ed	-0.5	54b
C(2)-C(6)	55	1.525	1.51	Xr	1.0	42				1.507	Ed	0.2	54c
	91	1.519	1.525	Xr	-0.3	43				1.517	Ed	-0.5	54d
	130	1.522	1.57	Xr	-3.1	44		53	1.514	1.499	Xr	1.0	55
	131	1.525	1.535	Xr	-0.7	17		114	1.509	1.525	Xr	-1.0	39
	132	1.525	1.534	Xr	-0.6	18		115	1.509	1.53	Xr	-1.4	40
	133	1.522	1.512	Xr	0.7	19	C(2)-C(9)	64	1.517	1.52	Xr	-0.2	56
C(3)-C(6)	54	1.537	1.507	Xr	2.0	45		89	1.516	1.498	Xr	1.2	57
C(4)-C(6)	75	1.560	1.566	Xr	-0.4	36		90	1.517	1.493	Xr	1.6	58

Table 9. (continued)

Bond ^a	Mole-b cule	r ^c calcd	r ^c exptl	Method ^d	Percent rel. error ^e	Ref. ^f	Bond ^a	Mole-b cule	r ^c calcd	r ^c exptl	Method ^d	Percent rel. error ^e	Ref. ^f
	85	1.502	1.51	Xr	-0.5	32	C(1)-C(7)	48	1.514	1.519	Ed	-0.3	71a
	142	1.501	1.504	Mw	-0.2	59				1.505	Xr	0.6	71b
C(3)-C(9)	76	1.522	1.54	Xr	-1.2	60		116	1.517	1.494	Xr	1.5	72
	85	1.511	1.52	Xr	-0.6	32		49	1.515	1.520	Ed	-0.3	73a
C(4)-C(9)	94	1.542	1.531	Xr	0.7	61				1.536	Xr	-1.4	73b
C(6)-C(9)	52	1.506	1.49	Xr	1.1	62	C(2)-C(7)	59	1.520	1.472	Xr	3.3	74
	53	1.514	1.499	Xr	1.0	55		83	1.520	1.476	Xr	3.0	75
	114	1.500	1.487	Xr	0.9	39	C(3)-C(7)	61	1.526	1.496	Xr	2.0	76
	115	1.501	1.44	Xr	4.2	40		62	1.526	1.507	Xr	1.3	76
C(1)-C(8)	33	1.505	1.520	Ed	-1.0	63a		60	1.527	1.510	Xr	1.1	77
			1.482	Xr	1.6	63b	C(4)-C(7)	63	1.542	1.531	Xr	0.7	78
	34	1.508	1.49	Xr	1.2	64	C(6)-C(7)	95	1.517	1.501	Xr	1.4	79
	73	1.507	1.46	Xr	3.2	65	C(6)-C(6)	108	1.481	1.489	Ed	-0.5	80a
C(2)-C(8)	32	1.517	1.503	Xr	0.9	66				1.507	Xr	-1.7	80b
	85	1.512	1.49	Xr	1.5	32				1.497	Xr	-1.1	80c
	88	1.514	1.517	Nd	-0.2	67		13	1.469	1.467	Xr	0.1	81a
	89	1.512	1.495	Xr	1.1	57				1.479	Xr	-0.7	81b
C(3)-C(8)	90	1.521	1.485	Xr	2.4	58		114	1.471	1.448	Xr	1.6	39
	124	1.511	1.523	Xr	-0.8	68		118	1.477	1.454	Xr	1.6	41
	125	1.525	1.527	Xr	-0.1	69		119	1.463	1.480	Xr	-1.1	82
	130	1.523	1.50	Xr	1.5	44		115	1.468	1.46	Xr	0.5	40
C(4)-C(8)	82	1.533	1.535	Xr	-0.1	66		117	1.472	1.478	Xr	-0.4	83
	86	1.531	1.515	Xr	1.1	70	C(10)-C(10)	18	1.466	1.463	Ed	0.2	84a
	94	1.532 ^c	1.517	Xr	1.0	61				1.467	Ed	-0.1	84b
		1.526 ^d	1.458		4.7			23a	1.466	1.458	Ed	0.5	85a

Table 9. (continued)

Bond ^a	Mole- cule ^b	r _{calcd} ^c	r _{exptl} ^c	Method ^d	Percent rel. error ^e	Ref. ^f	Bond ^a	Mole- cule ^b	r _{calcd} ^c	r _{exptl} ^c	Method ^d	Percent rel. error ^e	Ref. ^f
	23b	1.471	1.462	Ed	0.6	85b		16	1.339	1.330	Mw	0.7	21a
	24	1.479	1.470	Ed	0.6	25				1.342	Ed	-0.2	21b
	25	1.486	1.491	Ed	-0.3	26		17a	1.337	1.347	Ed	-0.7	22
	19	1.445	1.469	Mw	-1.6	28		17b	1.346	1.346	Ed	-0.1	22
	21	1.465 ^a	1.470	Mw	-0.5	86		18	1.338	1.341	Ed	-0.2	84a
		1.459 ^b	1.476		-1.2					1.344	Ed	-0.4	84b
	95	1.461 ^a	1.488	Ed	-1.9	87		19	1.335	1.342	Mw	-0.7	28
		1.453 ^b	1.516		-4.2			20	1.328	1.343	Ed	-1.1	95
C(6)-C(10)	134	1.473	1.485	Xr	-0.8	88		21	1.335 ^c	1.355	Mw	-1.5	86
	135	1.468	1.512	Xr	-2.9	89			1.336 ^d	1.349		-1.0	
	140	1.452	1.452	Xr	0.0	90		22a	1.340	1.336	Mw	0.3	27
C(9)-C(10)	67	1.467	1.470	Mw	-0.2	91		22b	1.338	1.342	Mw	-0.3	27
	87	1.480	1.462	Xr	1.2	24		23a	1.338 ^a	1.337	Ed	0.1	85a
	101	1.468	1.479	Ed	-0.7	92			1.338 ^b	1.368		-2.2	
	102	1.470	1.477	Xr	-0.5	93a		23b	1.338 ^c	1.336	Ed	0.1	85b
			1.481	Ed	-0.7	93b			1.345 ^b	1.362		-1.4	
C(10)=C(10)	14	1.337	1.337	Ed	0.0	94a		24	1.340	1.338	Ed	0.1	25
			1.333	Ed	0.3	94b		25	1.341	1.349	Ed	-0.6	26
			1.337	Ir	0.0	94c		67	1.338	1.345	Mw	-0.5	91
			1.339	Ra	-0.1	94d		71a	1.340	1.334	Ed	0.4	23
			1.335	Ed/Ir/ Ra	0.1	94e		71b	1.329	1.334	Ed	0.4	23
			1.314	Xr	1.8	94f		72a	1.344	1.349	Ed	-0.4	96
	15	1.338	1.336	Mw	0.1	20a		72b	1.344	1.344	Ed	0.0	96
			1.342	Ed	-0.3	20b		77	1.340	1.302	Xr	2.9	97
								80	1.340	1.316	Xr	1.8	30

Table 9. (continued)

Bond ^a	Mole- cule ^b	r ^c calcd	r ^c exptl	Method ^d	Percent rel. error ^e	Ref. ^f	Bond ^a	Mole- cule ^b	r ^c calcd	r ^c exptl	Method ^d	Percent rel. error ^e	Ref. ^f
C(6)=C(6)	81	1.340	1.297	Xr	2.3	31	C(5)≡C(5)	115	1.387	1.375	Xr	0.9	40
	85	1.340	1.32	Xr	1.5	32		116	1.389	1.354	Xr	2.6	72
	87	1.344	1.297	Xr	3.6	24		120	1.393	1.390	Mw	-0.2	105
	99	1.340 ^c	1.357	Ed	-1.3	87		40	1.207	1.203	Ir	0.3	106
		1.336 ^d	1.335		0.7			42	1.207	1.214	Ed	-0.6	48
	100	1.339	1.342	Ed	-0.4	29	C(X)-N(X)	104	1.207	1.209	Mw	-0.2	52a
	101	1.339	1.336	Ed	0.2	92				1.210	Ed	-0.2	52b
	109	1.341	1.342	Ed	-0.1	98		37	1.469	1.471	Mw	-0.2	107
	110	1.345	1.333	Ed	0.4	99		38	1.470	1.462	Mw	0.5	108a
	134	1.351	1.346	Xr	0.4	88				1.455	Ed	1.0	108b
	135	1.348	1.336	Xr	0.9	89	C(6)-N(2)	39	1.472	1.451	Mw	-1.4	109
	140	1.328	1.345	Xr	-1.3	90				1.455	Ed	1.2	108b
	10	1.391	1.398	Nd	-0.5	100a		91	1.476	1.472	Xr	0.3	43
			1.392	Xr	-0.1	13a		13	1.394	1.414	Xr	1.4	81a
			1.397	Ed	-0.4	100c				1.394	Xr	0.0	81b
			1.396	Ir	-0.4	100d		112	1.387	1.370	Mw	1.2	104
			1.397	Ra	-0.4	13b	C(10)-N(2)	115	1.393	1.375	Xr	1.3	40
	11	1.392	1.404	Xr	-0.9	101a		116	1.387	1.369	Xr	1.3	72
			1.406	Ed	-1.0	101b		117	1.388	1.383	Xr	0.4	83
	12	1.392	1.413	Xr	-1.5	102a		118	1.393	1.377	Xr	1.2	41
			1.411	Xr	-1.3	102b		137	1.372	1.369	Xr	0.2	110
C(6)=C(6)	111	1.386	1.361	Mw	1.8	103a		138	1.373	1.373	Xr	0.0	111
			1.322	Xr	4.8	103b		140	1.393	1.380	Xr	0.9	90
	112	1.385	1.382	Mw	0.2	104		137	1.344	1.349	Xr	-0.4	110
	114	1.387	1.356	Xr	2.2	39		138	1.346	1.327	Xr	1.4	111

Table 9. (continued)

Bond ^a	Mole- cule ^b	r ^c calcd	r ^c exptl	Method ^d	Percent rel. error ^e		Ref. ^f	Bond ^a	Mole- cule ^b	r ^c calcd	r ^c exptl	Method ^d	Percent rel. error ^e		Ref. ^f
C(1)-N(4)	34	1.513	1.50	Xr	0.9		64	C(2)-N(8)	62	1.476	1.466	Xr	0.7		76
	56	1.514	1.532	Xr	-1.2		112		63	1.477	1.454	Xr	1.6		78
	57	1.513	1.502	Xr	0.7		35		116	1.474	1.449	Xr	1.7		72
	73	1.516	1.52	Xr	-0.3		65	C(3)-N(8)	83	1.484	1.443	Xr	2.8		75
C(2)-N(4)	34	1.528	1.49	Xr	2.6		64	C(6)-N(8)	65	1.422	1.413	Xr	0.6		118a
	56	1.529	1.523	Xr	0.4		112				1.426	Xr	-0.3		118b
	57	1.528	1.511	Xr	1.1		35	C(7)-N(8)	46	1.356	1.352	Mw	0.3		119a
	74	1.517	1.513	Xr	0.3		113				1.368	Mw/Ed	-0.9		119b
C(3)-N(4)	128	1.508	1.490	Nd	1.2		14				1.300	Xr	4.3		119c
	54	1.518	1.498	Xr	1.3		45		47	1.361	1.366	Ed	-0.4		116
	73	1.547	1.55	Xr	-0.2		65		48	1.359	1.380	Ed	-1.5		71a
	129	1.513	1.497	Nd	0.9		15				1.334	Xr	1.9		71b
C(4)-N(4)	130	1.516	1.48	Xr	2.4		44		49	1.362	1.386	Ed	-1.7		73a
	74	1.528	1.504	Xr	1.7		113				1.290	Xr	5.6		73b
C(6)=N(5)	118	1.364	1.337	Xr	2.0		41		58	1.363	1.366	Xr	0.2		120
	120	1.367	1.338	Mw	2.2		105		59	1.360	1.312	Xr	3.7		74
	140	1.367	1.376	Xr	-0.6		90		60	1.365	1.320	Xr	3.4		77
	141	1.365	1.376	Xr	-0.8		114		61	1.361	1.318	Xr	3.3		76
C(1)-N(8)	136	1.366	1.345	Xr	1.6		115		62	1.365	1.319	Xr	3.5		76
	138	1.368	1.339	Xr	2.2		111		63	1.367	1.332	Xr	2.6		78
	47	1.473	1.459	Ed	1.0		116		65	1.354	1.330	Xr	1.8		118b
	49	1.472	1.469	Ed	0.2		73a				1.354	Xr	0.0		118a
			1.465	Xr	0.5		73b		66	1.367	1.344	Xr	1.7		117
	60	1.471	1.444	Xr	1.9		77		83	1.364	1.320	Xr	3.3		75
	66	1.471	1.467	Xr	0.3		117		116	1.364	1.326	Xr	2.9		72

Table 9. (continued)

Bond ^a	Mole- cule ^b	r _{calcd} ^c	r _{exptl} ^c	Method ^d	Percent rel. error ^e	Ref. ^f	Bond ^a	Mole- cule ^b	r _{calcd} ^c	r _{exptl} ^c	Method ^d	Percent rel. error ^e	Ref. ^f
C(10)=N(9)	137	1.330	1.326	Xr	0.3	110	C(2)-O	36	1.435	1.425	Mw	0.7	131a
	138	1.331	1.311	Xr	1.5	111				1.426	Mw	0.6	131b
C(6)-N(9)	137	1.374	1.378	Xr	-0.3	110				1.428	Mw	0.5	131c
	138	1.373	1.379	Xr	-0.4	111		75	1.435	1.452	Xr	-1.2	36
C(5)≡N(10)	43	1.154	1.155	Mw/Ir	-0.1	121		83	1.435	1.416	Xr	1.3	75
	44	1.154	1.157	Mw	-0.3	49a		88	1.433	1.420	Nd	0.9	67
			1.159	Ed	-0.4	49b		31	1.440	1.469	Xr	-2.0	132
	45	1.155	1.157	Mw	-0.2	50a		34	1.439	1.45	Xr	-0.8	64
			1.159	Mw	0.3	50b		97	1.435	1.412	Mw	1.6	130
	105	1.154	1.159	Mw	-0.4	52a		113	1.428	1.428	Ed	0.0	133a
C(1)-N(12)	121	1.492	1.49	Xr	0.1	112				1.428	Ed	0.0	133b
C(1)-N(13)	122	1.488	1.489	Mw	-0.1	123		124	1.436	1.422	Xr	1.0	68
C(6)-N(13)	123	1.502	1.486	Xr	1.1	124		125	1.436	1.418	Xr	1.3	69
C(1)-O	29	1.436	1.437	Mw	-0.1	125		126	1.437	1.413	Nd	1.7	142a
	35	1.432	1.425	Mw	0.5	126a		127	1.435 ^a	1.421	Nd	1.0	100b
			1.427	Mw	0.4	126b			1.436 ^b	1.417		1.3	
	51	1.431	1.423	Ed	0.6	127			1.436 ^c	1.423		0.9	
	54	1.432	1.406	Xr	1.8	45	C(3)-O	54	1.439	1.413	Xr	1.8	45
	55	1.432	1.43	Xr	0.1	42		57	1.441	1.443	Xr	-0.1	35
	66	1.430	1.410	Mw	1.4	128		83	1.442 ^a	1.448	Xr	-0.4	75
	50	1.436	1.491	Xr	-3.7	129			1.440 ^b	1.495		-3.7	
	97	1.430	1.412	Mw	1.3	130		85	1.436	1.41	Xr	1.8	32
	109	1.432	1.424	Ed	0.6	98		76	1.440	1.48	Xr	-2.7	60
	110	1.432	1.421	Ed	0.8	99		56	1.441	1.449	Xr	-0.6	112
	116	1.432	1.409	Xr	1.6	72		73	1.447	1.46	Xr	-0.9	65

Table 9. (continued)

Bond ^a	Mole- cule ^b	r _{calcd} ^c	r _{exptl} ^c	Method ^d	Percent rel. error ^e	Ref. ^f	Bond ^a	Mole- cule ^b	r _{calcd} ^c	r _{exptl} ^c	Method ^d	Percent rel. error ^e	Ref. ^f
C(4)-O	126	1.443	1.416	Nd	1.9	142	C(8)=O	31	1.351	1.330	Xr	2.3	132
	125	1.443 ^a	1.458	Xr	-1.7	69		32	1.353	1.343	Mw	0.7	136a
		1.443	1.420		1.6					1.26	Xr	7.3	136c
	127	1.443	1.422	Nd	1.5	100b				1.361	Ed	-0.6	136b
	78	1.443	1.459	Xr	-1.1	134		33	1.357	1.364	Ed	-0.5	63a
	82	1.445	1.407	Xr	2.7	66				1.318	Xr	3.0	63b
	127	1.443 ^d	1.408	Nd	2.5	100b		34	1.360	1.38	Xr	-1.4	64
C(6)-O		1.456 ^e	1.429		1.9			73	1.362	1.35	Xr	0.9	65
	51	1.387	1.361	Ed	1.9	127		82	1.359 ^b	1.310	Xr	3.7	66
	54	1.388	1.371	Xr	1.2	45			1.361 ^e	1.316		3.4	
	55	1.389	1.411	Xr	-1.5	42			1.360 ^e	1.298		4.7	
	56	1.388	1.386	Xr	0.1	112		85	1.360	1.32	Xr	3.0	32
	57	1.389	1.374	Xr	1.1	35		86	1.362	1.296	Xr	5.1	70
	68	1.379	1.379	Mw	0.0	135a		88	1.360	1.326	Nd	2.6	67
			1.364	Mw	1.1	135b		89	1.360	1.294	Xr	5.1	57
	116	1.387	1.379	Xr	0.6	72		90	1.360	1.317	Xr	3.3	58
	119	1.378	1.418	Xr	-2.8	82		93	1.359	1.367	Ed	-0.6	137a
C(10)-O	75	1.380	1.385	Xr	-0.4	36				1.324	Xr	2.6	137b
	111	1.369	1.362	Mw	0.5	103a		94	1.362 ^b	1.309	Xr	4.0	61
			1.368	Xr	0.1	103b			1.362 ^a	1.349		1.0	
	114	1.374	1.368	Xr	0.4	39		124	1.350	1.346	Xr	0.3	68
	109	1.360	1.353	Ed	0.1	98		125	1.357	1.324	Xr	2.5	69
C(8)-O	110	1.365	1.364	Ed	0.1	99		130	1.369	1.34	Xr	1.5	44
	29	1.355	1.344	Mw	0.8	125		29	1.224	1.200	Mw	2.0	125
	30	1.362	1.315	Xr	3.6	129		30	1.225	1.187	Xr	3.2	129

Table 9. (continued)

Bond ^a	Mole- cule ^b	r _{calcd} ^c	r _{exptl} ^c	Method ^d	Percent rel. error ^e	Ref. ^f	Bond ^a	Mole- cule ^b	r _{calcd} ^c	r _{exptl} ^c	Method ^d	Percent rel. error ^e	Ref. ^f
	31	1.225	1.212	Xr	1.1	132		27	1.223	1.216	Mw	0.6	53a
	32	1.224	1.202	Mw	1.8	136a				1.207	Mw/Ed	1.3	53b
			1.23	Xr	0.5	136c		28	1.225	1.222	Mw	0.2	54a
			1.217	Ed	0.6	136b				1.210	Mw/Ed	1.2	54b
	33	1.226	1.214	Ed	1.0	63a				1.210	Ed	1.2	54c
			1.220	Xr	0.5	63b				1.211	Ed	1.1	54d
	34	1.225	1.18	Xr	3.8	64		52	1.224	1.23	Xr	-0.5	62
	73	1.225	1.25	Xr	-2.0	65		53	1.224	1.216	Xr	0.7	55
	82	1.226 ^{b1}	1.210	Xr	1.3	66		67	1.222	1.219	Mw	0.2	91
		1.226 ^{c1}	1.239		-1.0			76	1.226	1.23	Xr	-0.3	60
		1.228 ^{a1}	1.202		2.2			85	1.225	1.16	Xr	5.6	32
	85	1.226	1.19	Xr	3.0	32		87	1.222	1.185	Xr	3.1	24
	86	1.227	1.232	Xr	-0.5	70		89	1.225	1.212	Xr	1.1	57
	88	1.227	1.226	Nd	0.1	67		90	1.225	1.237	Xr	-1.0	58
	89	1.226	1.216	Xr	0.7	57		94	1.227	1.225	Xr	0.8	61
	90	1.227	1.240	Xr	-1.0	58		101	1.222	1.207	Ed	1.2	92
	93	1.226	1.211	Ed	1.2	137a		102	1.223	1.222	Xr	0.1	93a
			1.225	Xr	0.0	137b				1.225	Ed	-0.2	93b
	94	1.227 ^c	1.197	Xr	2.5	61		114	1.223	1.210	Xr	1.1	39
		1.227 ^f	1.215		1.0			115	1.223	1.24	Xr	-1.4	40
	124	1.223	1.194	Xr	2.4	68	C(7)=O	46	1.222	1.219	Mw	0.2	119a
	125	1.224	1.208	Xr	1.3	69				1.212	Mw/Ed	0.8	119b
	130	1.227	1.17	Xr	4.9	44				1.255	Xr	-2.6	119c
C(9)=O	26	1.221	1.208	Mw	1.1	138		47	1.222	1.219	Ed	0.2	116
			1.209	Ed	1.0	54d		48	1.224	1.220	Ed	0.3	71a

Table 9. (continued)

Bond ^a	Mole- cule ^b	r _{calcd} ^c	r _{exptl} ^c	Method ^d	Percent rel. error ^e	Ref. ^f	Bond ^a	Mole- cule ^b	r _{calcd} ^c	r _{exptl} ^c	Method ^d	Percent rel. error ^e	Ref. ^f
			1.260	Xr	-2.9	71b		26	1.095	1.116	Mw	-1.9	138
	49	1.224	1.225	Ed	0.1	73a		29	1.095	1.101	Mw	-0.5	125
			1.236	Xr	-1.0	73b		32	1.095	1.097	Mw	-0.2	136a
	58	1.224	1.217	Xr	0.6	120				1.106	Ed	-1.0	136b
	59	1.224	1.282	Xr	-4.5	74		46	1.097	1.098	Mw	-0.1	119a
	60	1.225	1.239	Xr	-1.1	77				1.125	Mw/Ed	-2.5	119b
	61	1.225	1.229	Xr	-0.3	76	H-C(6)	10	1.087	1.090	Nd	-0.3	100a
	62	1.225	1.241	Xr	-1.3	76				1.083	Ir	0.4	100d
	63	1.226	1.233	Xr	-0.6	78				1.084	Ra	0.3	13b
	65	1.224	1.226	Xr	-0.2	118b		112		1.077	Mw		104
			1.219	Xr	0.4	118a		111	1.086	1.076	Mw	0.9	103a
	66	1.224	1.263	Xr	-3.1	117		120	1.087	1.083	Mw	0.4	105
	116	1.224	1.236	Xr	-1.0	72	H-C(5)	40	1.057	1.061	Ir	-0.4	106
	83	1.224	1.281	Xr	-4.4	75		41	1.057	1.056	Mw	-0.1	47a
C(13)=O	86	1.252	1.252	Xr	0.0	70		43	1.057	1.063	Mw/Ir	-0.6	121
	128	1.251	1.261	Nd	-6.8	14	H-C(10)	14	1.086	1.103	Ed	-1.5	94a
	129	1.252	1.258	Nd	-0.5	15				1.084	Ed	0.2	94b
N(12)=O	121	1.223	1.22	Mw	0.2	122				1.086	Ra	0.0	94d
N(13)=O	122	1.224	1.224	Mw	0.0	123				1.090	Ed/Ir/Ra	-0.4	94e
	123	1.222	1.208	Xr	1.2	124		15	1.086	1.087	Mw	-0.1	20a
			1.227	Mw	-0.4	139		16	1.085	1.088	Mw	-0.3	21a
H-C(X)	1	1.097	1.102	Ir/Ra	-0.5	148a				1.095	Ed	-0.9	21b
			1.108	Ir	-1.0	148b		18	1.087	1.090	Ed	-0.3	84a
			1.112	Ed	-1.3	148c				1.094	Ed	-0.6	84b
	2	1.098	1.094	Mw	0.4	149a		21	1.086	1.079	Mw	0.6	86

Table 9. (continued)

Bond ^a	Mole- cule ^b	r ^c _{calcd}	r ^c _{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f	Bond ^a	Mole- cule ^b	r ^c _{calcd}	r ^c _{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f
H-N(X)	37	1.018	1.010	Mw	0.8	107	H-N(4)	128	1.041	1.046	Nd	-0.5	14
	38	1.020	1.019	Mw	0.1	108a		129	1.040	1.039	Nd	0.1	15
	46	1.018	1.002	Mw	1.6	119a	H-O	106	0.958	0.957	Ir	0.1	141
			1.027	Mw/Ed	-0.9	119b		32	0.960	0.972	Mw	-1.2	136a
	48	1.018	1.022	Ed	-0.4	71a				0.984	Ed	-2.4	136b
	112	1.017	0.996	Mw	2.2	104		35	0.961	0.945	Mw	1.7	126a
107	1.016	1.012	Ir	0.4	140				0.956	Mw	0.5	126b	

^aSee Table 1 for the description of bond types. ^bSee Fig. 2. ^cUnit is in angstrom. Superscripts refer to the particular bonds of a molecule in Fig. 2. ^dThe codes adopted for the experimental methods are: Infrared(Ir), Raman(Ra), Electron diffraction(Ed), Neutron diffraction(Nd), X-ray Diffraction(Xr), Microwave(Mw). ^eRelative error(%)=100x(calculated value-experimental value)/experimental value. ^fReference for the experimental geometrical data.

Table 10. Calculated bond angles

Angle ^a	Mole- cule ^b	θ^c_{calcd}	θ^c_{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f	Angle ^a	Mole- cule ^b	θ^c_{calcd}	θ^c_{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f
C(X)-C(2)-C(X)	2	111.9	112.4	Mw	-0.4	149a	C(X)-C(3)-C(X)	57	108.7	110.2	Xr	-1.4	35
			112.0	Mw/Ed	-0.1	149b		60	111.1	110.7	Xr	0.4	77
	3	111.9	112.4	Ed	-0.4	150a		61	110.9	110.3	Xr	0.5	76
			112.2	Ed	-0.3	150b		62	111.0	110.0	Xr	0.9	76
	5	111.9	112.9	Ed	-0.9	154a		70	117.0	116.0	Ed	0.9	144d
			112.0	Xr	-0.1	154b		73	112.3 ^{α}	114	Xr	-1.5	65
	6	112.0	111.9	Ed	0.1	154a			111.8 ^{β}	111		0.7	
			114	Xr	-1.8	155		80	111.9 ^{α^*}	112.0	Xr	-0.9	30
	8	111.2	111.6	Ed	-0.4	143a			111.6 ^{β^*}	111.8		-0.2	
			111.1	Ed	0.1	143b		81	111.9 ^{β^*}	112.0	Xr	-0.1	31
			111.3	Xr	-0.1	143c			111.7 ^{α^*}	112.8		-0.1	
	113	104.3	100.3	Ed		133a		83	115.7 ^{α}	116.0	Xr	-0.3	75
			104.1						116.1 ^{β}	116.7		-0.5	
	116	113.8	113.9	Xr	-0.1	72			113.2 ^{γ}	114.8		-1.4	
	130	115.2	113	Xr	1.9	44		85	112.5	113.7	Xr	-1.1	32
	131	112.0	110.3	Xr	1.5	17		89	110.7	111.1	Xr	-0.4	57
	132	112.5	112.9	Xr	-0.4	18		90	111.0	110.8	Xr	0.0	58
C(X)-C(3)-C(X)	133	114.3 ^{α}	114.8	Xr	-0.4	19		124	102.3 ^{α_1}	101.8	Xr	0.5	68
		116.6 ^{β}	116.8		-0.2				98.7 ^{α_2}	100.9		-2.2	
	4	110.5	111.2	Mw	-0.6	151a			117.4 ^{α_3}	115.6		1.6	
			110.8	Mw/Ed	-0.3	151b		125	114.3 ^{α}	113.5	Xr	1.1	69
	54	110.9 ^{α}	111.9	Xr	-9.9	45			107.3 ^{β}	108.8		-0.9	
		114.3 ^{β}	114.0		0.3				107.8 ^{γ}	110.7		-2.6	
	55	110.1	112	Xr	-1.7	42			114.6 ^{δ}	114.7		-0.1	
	56	109.3	107.8	Xr	1.4	112		126	111.7 ^{α}	111.1	Nd	0.5	142

Table 10. (continued)

Angle ^a	Mole- cule ^b	θ^c_{calcd}	θ^c_{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f	Angle ^a	Mole- cule ^b	θ^c_{calcd}	θ^c_{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f
		109.0 ^{β}	109.8		-0.7					116.0	Mw/Ed	0.4	54b
		110.9 ^{γ}	111.2		-0.3		C(2)-C(9)-C(2)	89	115.8	117.9	Xr	-1.8	57
		112.7 ^{δ}	111.6		1.0			90	115.9	117.3	Xr	-1.2	58
	127	100.0 ^{α}	102.3	Nd	-2.2	100b		142	113.1	110.5	Mw	2.4	59
		102.5 ^{β}	102.4		0.1		C(3)-C(9)-C(3)	76	117.0	118	Xr	-0.8	60
		115.9 ^{γ}	115.0		0.8		C(4)-C(9)-C(4)	94	122.6	123.0	Xr	-0.3	61
		115.9 ^{δ}	114.9		0.9		C(1)-C(9)-C(6)	53	120.6	119.0	Xr	1.3	55
		111.2 ^{α_1}	111.0		0.2			114	119.2	120.1	Xr	-0.7	39
		108.5 ^{β_1}	108.1		0.4			115	119.2	120.7	Xr	-1.2	40
		112.6 ^{γ_1}	111.9		0.6		C(6)-C(9)-C(6)	52	120.0	122.0	Xr	-1.6	62
		111.7 ^{δ_1}	110.8		0.8		C(10)-C(9)-C(10)	102	117.1	117.8	Xr	-0.6	93a
	129	110.1	112.2	Nd	-1.9	15				118.1	Ed	-0.8	93b
	130	112.1	116	Xr	-3.4	44	C(X)-C(10)-C(X)	16	114.8	115.3	Mw	-0.4	21a
C(X)-C(4)-C(X)	69	109.5	109.5	Ed	0.0	153b				115.6	Ed	-0.7	21b
	82	108.0	107.9	Xr	0.1	66		87	117.8	120.4	Xr	-2.2	24
	86	109.4	109.5	Xr	-0.1	70		99	87.8	86.9	Ed	1.0	87
	94	109.5	109.4	Xr	0.2	61	C(6)-C(6)-C(9)	115	126.2	126.9	Xr	-0.6	40
	63	109.5	109.4	Xr	0.1	78	C(1)-C(6)=C(6)	57	121.6 ^{α}	119.9	Xr	1.4	35
	70	113.9 ^{t_{qm}}	113.0	Ed	0.8	144d			118.2 ^{β}	121.8		-3.0	
		104.7 ^{in_{qm}}	105.8		-1.0			75	118.4 ^{α_1}	119.4	Xr	-0.8	36
	74	107.7	108.1	Xr	-0.4	113			123.0 ^{α_2}	122.8		0.2	
	78	110.9	112.0	Xr	-1.0	134			118.7 ^{β_1}	119.4		-0.6	
	84	108.6	108.8	Xr	-0.2	46			122.0 ^{β_2}	121.6		0.3	
	79	109.3	109.4	Xr	-0.1	33			126.9 ^{γ_1}	123.9		2.4	
C(1)-C(9)-C(1)	28	116.5	117.2	Mw	-0.6	54a			112.4 ^{γ_2}	116.0		-3.1	

Table 10. (continued)

Angle ^a	Mole- cule	θ^c_{calcd}	θ^c_{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f	Angle ^a	Mole- cule	θ^c_{calcd}	θ^c_{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f
C(2)-C(6)=C(6)	79	130.5 ^{α}	130.3	Xr	0.2	33	C(7)-C(6)=C(6)	53	121.1	120.3	Xr	0.7	65
		114.0 ^{β}	114.7		-0.6			114	127.9	125.6	Xr	1.8	39
	92	121.6 ^{α}	122.0	Xr	-0.3	37		115	127.3	125.6	Xr	1.4	40
		119.0 ^{β}	119.4		-0.3			95	120.0 ^{α_1}	118.2	Xr	1.5	79
	98	121.4 ^{α}	121.1	Xr	0.2	38			120.4 ^{α_2}	121.7		-1.1	
		119.1 ^{β}	119.1		0.0		C(X)-C(10)=C(10)	15	122.0	124.3	Mw	-1.9	20a
	118	121.2	121.5	Xr	-0.2	41				124.3	Ed	-1.9	20b
	55	122.4 ^{α_1}	123	Xr	-0.5	42		16	122.6	122.4	Mw	0.2	21a
		117.6 ^{α_2}	121		-2.8			17a	121.2	123.8	Ed	-2.1	22
		122.4 ^{β_1}	123		-0.5			17b	125.9	125.4	Ed	0.4	22
		117.5 ^{β_2}	119		-1.3			18	121.6	123.3	Ed	-1.4	84a
	91	120.3	121.1	Xr	-0.7	43				122.9	Ed	-1.1	84b
	130	120.4 ^{α}	118	Xr	2.0	44		19	112.4 ^{α}	109.3	Ed	2.8	28
		120.4 ^{β}	121		-0.5				108.4 ^{β}	109.4		-0.9	
	131	121.9 ^{α}	123.6	Xr	-1.4	17		21	109.0 ^{α}	107.7	Mw	1.2	86
		119.0 ^{β}	116.7		2.0				106.7 ^{β}	109.0		-0.3	
	132	119.8	123.4	Xr	-0.5	18			127.3 ^{γ}	126.7		0.9	
	133	120.5	121.6	Xr	-0.9	19		22b	122.2	125.4	Mw	-2.6	27
								22a	124.0	126.7		-2.1	27
C(3)-C(6)=C(6)	54	119.9 ^{γ_1}	120.8	Xr	-0.8	45		23a	122.7 ^{α_1}	121.7	Mw	0.0	85a
		121.2 ^{γ_2}	119.2		1.7				122.7 ^{α_2}	124.4		-2.2	
C(4)-C(6)=C(6)	75	119.8 ^{δ_1}	118.2	Xr	1.4	36		23b	121.2 ^{α_1}	122.1	Mw	-0.7	85b
		124.5 ^{δ_2}	127.2		-2.1				125.3 ^{α_2}	125.7		-0.3	
C(10)-C(6)=C(6)	134	119.9	120.7	Xr	-0.7	88		24	121.5	120	Ed	1.4	25
	135	119.0	120.1	Xr	-0.9	89		25	123.4 ^{α_1}	122.0	Ed	1.4	26
C(9)-C(6)=C(6)	52	120.4	119.8	Xr	0.5	62							

Table 10. (continued)

Angle ^a	Mole- cule ^b	θ^c calcd	θ^c exptl	Method ^d	Percent rel. error ^e	Ref. ^f	Angle ^a	Mole- cule ^b	θ^c calcd	θ^c exptl	Method ^d	Percent rel. error ^e	Ref. ^f
		116.0 ^{α_2}	117.9		-1.6				118.3 ^Y				
	72a	123.0	124.5	Ed	-1.2	96		136	119.8	116.3	Xr	3.0	115
	72b	123.0	124.9	Ed	-1.5	96		138	121.9	117.9	Xr	3.4	111
	77	124.6	127.7	Xr	-2.4	97		140	108.7 ^{α}	107.9	Xr	0.7	90
	80	122.3 ^{α_1}	125.8	Xr	-3.5	30			125.9 ^{β}	127.1		-0.9	
		122.0 ^{α_2}	125.3		-2.6		C(X)-C(2)-N(X)	62	114.4	113.3	Xr	1.0	76
	81	122.1 ^{α_1}	127.2	Xr	-4.0	31		63	113.8	113.7	Xr	0.1	78
		121.1 ^{α_2}	125.9		-3.8			116	113.5	110.9	Xr	2.3	72
	85	122.2 ^{α_1}	126.9	Xr	-3.7	32		128	112.7	111.8	Nd	0.8	14
		121.8 ^{α_2}	126.6		-3.8		C(X)-C(3)-N(X)	55	113.0 ^{Y₁}	110	Xr	2.7	42
	87	124.6	127.1	Xr	-2.0	24			111.2 ^{Y₂}	108		3.0	
	99	136.2 ^{α_1}	135.7	Ed	0.4	87		83	109.5 ^{δ_1}	108.6	Xr	0.8	75
		92.2 ^{α_2}	93.1		-1.0				110.7 ^{δ_2}	115.0		-3.7	
	100	122.6	123.4	Ed	-0.6	29		129	113.0	110.0	Nd	2.7	15
	101	121.7	122.7	Ed	-0.8	92	C(X)-C(4)-N(X)	74	107.0	111.8	Xr	-4.3	113
	110	124.3 ^{α_1}	124.2	Ed	0.1	99			113.1	116.5		-2.9	
		121.6 ^{α_2}	123.1		-1.2				112.5	102.9		9.3	
	134	120.9 ^{α_1}	120.8	Xr	0.1	88	C(2)-C(2)-N(4)	34	117.8	119	Xr	-1.0	64
		123.9 ^{α_2}	125.8		-1.5			74	109.3	106.0	Xr	3.1	113
	135	118.8	118.9	Xr	-0.1	89	C(3)-C(2)-N(4)	56	117.5	114.4	Xr	2.7	112
C(6)=C(6)=C(6)	10	120.0	120.0	Xr	0.0	13a		57	117.7	115.4	Xr	2.0	35
	79	128.6 ^Y	129.8	Xr	-0.9	33	C(1)-C(3)-N(4)	54	108.9	109.6	Xr	-0.6	45
		115.3 ^{δ}	115.0		0.3			73	113.1	108	Xr	4.7	65
	120	122.8 ^{α}	123.8	Mw	-0.8	105		129	108.4	109.8	Nd	-1.3	15
		119.7 ^{β}	118.5		1.0		C(3)-C(3)-N(4)	54	111.3	107.8	Xr	3.2	45

Table 10. (continued)

Angle ^a	Mole- cule	^b $\theta_{\text{calcd}}^{\text{c}}$	$\theta_{\text{exptl}}^{\text{c}}$	Method ^d	Percent rel. error ^e	Ref. ^f	Angle ^a	Mole- cule	^b $\theta_{\text{calcd}}^{\text{c}}$	$\theta_{\text{exptl}}^{\text{c}}$	Method ^d	Percent rel. error ^e	Ref. ^f
C(1)-C(7)-N(8)	73	115.2	113	Xr	1.9	65	C(6)=C(6)-N(13) C(6)=C(6)-N(8)	112	108.9	107.7	Mw	1.1	104
	48	114.9	115.1	Ed	-0.2	71a		115	108.5	108.3	Xr	1.1	40
			117.2	Xr	-2.0	71b		117	103.6 ^{a1}	108.1	Xr	0.5	83
	49	114.5	114.1	Ed	0.4	73a			109.3 ^{a2}	109.1		0.1	
			116.5	Xr	-1.7	73b		137	106.5	106.3	Xr	0.2	110
	58	117.1	117.2	Xr	-0.1	120		138	106.3	105.1	Xr	1.1	111
	65	115.7	117.7	Xr	-1.7	118b		140	106.3	107.9	Xr	-1.5	90
			115.3	Xr	0.3	118a		123	121.4	117	Xr	3.8	124
	66	115.9	118.5	Xr	-2.2	117		58	121.3	121.3	Xr	0.0	120
	116	115.6	117.2	Xr	-1.4	72		65	120.1 ^{a1}	123.8	Xr	-3.1	118a
C(2)-C(7)-N(8)	59	114.7	116.3	Xr	-1.4	74			120.3 ^{a2}	116.6		3.1	
	83	113.9	116.6	Xr	-2.3	75		66	120.3 ^{a1}	118.2	Xr	1.8	117
C(3)-C(7)-N(8)	50	115.6	117.4	Xr	-1.5	77			120.2 ^{a2}	118.2		1.7	
	61	116.0	117.3	Xr	-1.1	76	C(6)=C(6)-N(9)	137	109.3	109.8	Xr	0.0	110
	62	115.4	117.5	Xr	-1.8	76		138	110.2	109.6	Xr	0.5	111
C(4)-C(7)-N(8)	63	116.9	116.8	Xr	0.1	78	C(10)-C(6)=N(5)	140	109.8	109.8	Xr	0.9	90
C(6)-C(7)-N(8)	95	114.3	117.5	Xr	-2.7	79	C(6)=C(6)-N(5)	120	122.5	123.8	Mw	-0.1	105
C(1)-C(6)-N(2)	115	123.3	119.4	Xr	3.3	40		118	124.5	124.5	Xr	-0.4	41
C(6)-C(6)-N(2)	117	123.7	120.0	Xr	3.1	83		136	121.5	122.6	Xr	-1.1	115
C(6)=C(6)-N(2)	13	109.7	108.8	Xr	0.8	81a		138	122.5 ^{a1}	123.9	Xr	-1.5	111
			109.7	Xr	0.0	81b			118.6 ^{a2}	118.9		-0.3	
	115	108.6 ^{a1}	106.9	Xr	1.6	72		140	124.5	125.0	Xr	-0.4	90
		109.6 ^{a2}	110.3		-0.6			141	109.2	110.0	Xr	0.7	114
	118	109.2 ^{a1}	108.2	Xr	-0.9	41	C(X)-C(X)-O	36	109.3	107.3	Mw	1.9	131a
		109.8 ^{a2}	110.1		-0.3					107.4	Mw	1.8	131b

Table 10. (continued)

Angle ^a	Mole- ^b cule	θ_{calcd}^c	θ_{exptl}^c	Method ^d	Percent rel. error ^e	Ref. ^f	Angle ^a	Mole- ^b cule	θ_{calcd}^c	θ_{exptl}^c	Method ^d	Percent rel. error ^e	Ref. ^f
			107.6	Mv	1.6	131c			109.8 ^{δ_2}	109.6		0.2	
	75	109.8	109.5	Xr	0.3	36	83	109.2 ^{ϵ_1}	107.0	Xr		2.1	75
	78	108.4 ^{α_1}	106.4	Xr	1.9	134		110.9 ^{ϵ_2}	108.3			2.4	
		107.3 ^{α_2}	106.6		0.7		76	110.2 ^{α_1}	104	Xr		6.0	60
		108.6 ^{α_3}	107.4		1.1			110.1 ^{α_2}	105			4.9	
	82	107.4 ^{α_1}	106.4	Xr	0.9	66	85	109.0 ^{β_1}	108.8	Xr		0.2	32
		107.9 ^{α_2}	112.1		-3.4			109.7 ^{β_2}	107.4			2.1	
		110.3 ^{α_3}	109.8		0.5			113.5 ^{γ_1}	114.1			-0.5	
	88	111.6	112.1	Nd	-0.4	67		113.2 ^{γ_2}	115.5			-2.0	
	83	111.2	112.4	Xr	-1.4	75	124	105.9 ^{β_1}	103.6	Xr		2.2	68
	97	109.8	108.0	Mv	1.7	130		113.5 ^{β_2^*}	112.3			1.1	
	113	105.9	103.7-	Ed		133a		112.0 ^{β_3^*}	109.8			2.0	
			107.4					110.1 ^{β_4^*}	109.4			0.6	
			104.0-	Ed		133b	125	110.6	109.5	Xr		1.0	69
			107.5					113.5 ^{δ}	111.0			2.3	
	126	110.8	110.4	Xr	0.4	142	126	110.0 ^{ϵ_1}	110.1	Nd		-0.1	142
	125	112.3	113.1	Xr	-0.7	69		110.7 ^{ϵ_2}	108.7			1.8	
	127	112.1 ^{ϵ_1}	111.2	Nd	0.8	13	127	111.8 ^{η_1}	110.3	Nd		1.4	100b
		112.8 ^{ϵ_2}	113.0		-0.2			110.9 ^{η_2}	110.9			0.0	
		112.5 ^{ϵ_3}	111.5		0.9			112.4 ^{η_3}	110.7			1.5	
C(X)-C(3)-O	54	111.8 ^{δ_1}	112.1	Xr	-0.3	45		107.9 ^{η_4}	105.6			2.2	
		112.3 ^{δ_2}	105.7		6.2		C(2)-C(10)-O	110	111.6	113.3	Ed	-1.5	99
	56	110.0 ^{α_1}	105.4	Xr	4.4	100b	C(X)-C(8)-O	30	111.2	112.5	Xr	-1.2	129
		109.5 ^{α_1}	110.4		-0.8			33	111.5	110.6	Ed	0.8	63a
	57	110.0 ^{δ_1}	105.7	Xr	4.1	35			113.8	Xr		-2.0	63b

Table 10. (continued)

Angle ^a	Mole- cule ^b	θ_{calcd}^c	θ_{exptl}^c	Method	Percent d rel. error ^e	Ref. ^f	Angle ^a	Mole- cule ^b	θ_{calcd}^c	θ_{exptl}^c	Method	Percent d rel. error ^e	Ref. ^f
C(6)=C(6)-O	31	111.1	113.2	Xr	-1.9	132	C(10)=C(10)-O	54	118.8 ^{δ_4}	115		3.3	
	34	111.2	108	Xr	3.0	64		56	125.3 ^{β_1}	124.9	Xr	0.3	112
	82	112.4 ^{β_1}	112.5	Xr	-0.1	66			116.2 ^{β_2}	112.5		3.2	
		111.4 ^{β_2}	114.1		-2.4			57	123.9 ^{γ_1}	124.4	Xr	-0.4	35
		112.1 ^{β_3}	111.4		0.6				117.5 ^{γ_2}	115.0		2.2	
	85	111.4	112.7	Xr	-1.3	32		75	117.1 ^{ϵ_1}	118.0	Xr	-0.8	36
	88	111.2	112.4	Ne	-1.1	67			113.9 ^{ϵ_2}	117.7		1.9	
	89	111.3	113.9	Xr	-2.3	57		116	123.8 ^{β_1}	124.4	Xr	-0.5	72
	90	111.9	116.8	Xr	-4.2	58			116.9 ^{β_2}	114.7		1.9	
	93	111.3	111.2	Ed	0.1	137a		119	110.7	112.9	Xr	-1.9	82
			114.0	Xr	-2.4	137b		111	111.3	110.7	Mw	0.5	103a
	94	112.2 ^{α_1}	112.5	Xr	-0.3	61				110.1	Xr	1.1	103b
		112.2 ^{α_2}	112.7		-0.4			114	112.0	110.0	Xr	1.8	39
	73	111.0	113	Xr	-1.8	65		109	124.4	123.3	Ed	0.8	98
	124	110.7	109.2	Xr	1.4	68		110	124.1	122.5	Ed	1.3	99
	125	117.3	119.8	Xr	-2.1	69		27	122.9	123.9	Mw	-0.8	53a
	130	111.7	109	Xr	2.5	44				124.2	Mw/Ed	-1.0	53b
	86	112.9	115.2	Xr	-2.0	70		28	121.3	121.4	Mw	0.3	54a
	54	117.5 ^{ϵ_1}	114.5	Xr	2.6	45				122.0	Mw/Ed	-0.2	54b
		124.4 ^{ϵ_2}	126.4		-1.6			53	119.4	121.0	Ed	-1.3	55
		118.3 ^{ϵ_3}	116.3		2.2			114	122.5	120.1	Xr	1.8	39
		122.2 ^{ϵ_4}	125.0		-2.2			115	122.2	118.7	Xr	3.0	40
	55	123.1 ^{δ_1}	121	Xr	1.7	42		39	122.1	121.0	Xr	0.9	57
		118.8 ^{δ_2}	115		3.3			90	122.2	121.3	Xr	0.7	58
		123.1 ^{δ_3}	123		0.1			85	123.2	125.3	Xr	-1.7	32
C(2)-C(9)=O							C(1)-C(9)=O						

Table 10. (continued)

Angle ^a	Mole- cule ^b	θ_{calcd}^c	θ_{exptl}^c	Method ^d	Percent rel. error ^e	Ref. ^f	Angle ^a	Mole- cule ^b	θ_{calcd}^c	θ_{exptl}^c	Method ^d	Percent rel. error ^e	Ref. ^f
C(3)-C(9)=O	76	121.6 ^{B1}	119	Xr	2.2	60		94	125.2 ^{Y1}	128.6	Xr	-2.6	61
		121.4 ^{B2}	122		-0.5				125.4 ^{Y2}	125.9		-0.4	
	85	124.4	126.3	Xr	-1.5	32		73	124.2	126	Xr	-1.4	65
C(4)-C(9)=O	94	117.7 ^{B1}	118.7	Xr	-0.8	61		124	127.6	128.5	Xr	-0.7	68
		119.7 ^{B2}	118.2		1.3			125	125.0	120.7	Xr	3.6	69
C(6)-C(9)=O	52	120.0	119.7	Xr	0.3	62		130	125.4	127	Xr	-1.3	44
	53	120.0	120.0	Xr	0.0	55	C(1)-C(7)=O	48	122.5	123.0	Ed	-0.4	71a
C(10)-C(9)=O	67	122.7	123.3	Mw	-0.5	91				119.7	Xr	2.3	71b
	87	126.2	124.9	Xr	1.0	24		49	121.8	124.1	Ed	-1.9	73a
	101	122.7	123.6	Ed	-0.7	92				120.5	Xr	1.2	73b
C(X)-C(8)=O	30	124.4	126.6	Xr	-1.7	129		58	120.5	121.7	Xr	-1.0	120
	33	124.7	126.6	Ed	-1.5	63a		65	121.3	120.4	Xr	0.7	118b
			124.2	Xr	0.4	63b				121.6	Xr	-0.2	118a
	31	124.4	122.8	Xr	1.3	132	C(2)-C(7)=O	59	123.4	129.0	Xr	-4.3	74
	34	124.4	129	Xr	-3.6	64		83	122.7	121.6	Xr	0.9	75
	82	125.5 ^{Y1}	123.0	Xr	2.0	66	C(3)-C(7)=O	60	121.7	121.2	Xr	0.4	77
		125.8 ^{Y2}	122.5		2.7			61	122.3	120.5	Xr	1.5	76
		124.5 ^{Y3}	125.7		-1.0			62	121.7	121.2	Xr	0.4	76
	85	125.5	123.6	Xr	1.5	32	C(4)-C(7)=O	63	122.2	122.1	Xr	0.1	78
	86	125.1	122.3	Xr	2.3	70	C(6)-C(7)=O	95	122.2	120.5	Xr	1.4	79
	88	125.5	122.7	Nd	2.3	67	C(2)-C(11)=O	128	117.5	117.3	Nd	0.2	14
	89	125.4	122.7	Xr	2.3	57	C(3)-C(11)=O	129	118.3 ^{Q1}	118.3	Nd	0.0	15
	90	125.0	123.0	Xr	1.6	58			117.4 ^{Q2}	116.0		1.2	
	93	125.4	126.7	Ed	-1.0	137a	N(8)-C(7)=O	46	124.8	121.5	Xr	2.7	119c
			124.0	Xr	1.1	137b				124.7	Mw	0.1	119a

Table 10. (continued)

Angle ^a	Mole- cule ^b	θ_c θ_{calcd}	θ_c θ_{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f	Angle ^a	Mole- cule ^b	θ_c θ_{calcd}	θ_c θ_{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f
			125.0	Mw/Ed	-0.2	119b		33	123.8	122.8	Ed	0.8	63a
	47	126.4	124.6	Ed	1.4	116				122.0	Xr	1.5	63b
	48	122.7	122.0	Ed	0.6	71a		31	124.5	123.9	Xr	0.5	132
			123.1	Xr	-0.3	71b		34	124.5	123	Xr	1.2	64
	49	123.7	121.8	Ed	1.6	73a		82	122.1 ^{δ_1}	124.4	Xr	-1.8	66
			123	Xr	0.6	73b			122.9 ^{δ_2}	123.4		-0.4	
	58	122.4	121.0	Xr	1.1	120			123.4 ^{δ_3}	122.9		0.6	
	59	122.0	114.4	Xr	6.6	74		85	123.2	123.7	Xr	-0.4	32
	60	122.7	121.2	Xr	1.2	77		86	122.0	122.5	Xr	-0.4	70
	61	121.7	122.1	Xr	-0.3	76		88	123.3	122.8	Nd	0.4	67
	62	122.9	123.6	Xr	-0.7	76		89	123.3	123.4	Xr	-0.1	57
	63	120.9	121.1	Xr	0.2	78		90	123.1	120.8	Xr	1.9	58
	65	122.9	123.1	Xr	-0.2	118b		93	123.4	122.1	Ed	1.1	137a
			121.7	Xr	1.0	118a				122.0	Xr	1.1	137b
	66	123.0	117.0	Xr	5.1	117		94	122.6 ^{δ_1}	118.9	Xr	3.2	61
	83	123.4	121.5	Xr	1.6	75			122.3 ^{δ_2}	121.3		0.9	
	95	123.5	122.1	Xr	1.1	79		73	124.8	122	Xr	2.3	65
	116	123.2	121.1	Xr	1.7	72		124	121.7	122.4	Xr	-0.6	68
N(2)-C(10)=N(9)	117	112.9	111.3	Xr	1.4	110		125	117.5	119.4	Xr	-1.6	69
	118	113.0	115.1	Xr	1.8	111		130	122.9	124	Xr	-0.9	44
N(9)-C(6)=N(5)	138	127.7	126.5	Xr	0.9	111	O=C(13)=O	128	125.0	125.4	Nd	-0.3	14
N(5)-C(6)=N(5)	136	128.6	128.2	Xr	0.3	115		129	124.3	125.7	Nd	-1.1	15
	138	129.4	127.9	Xr	1.2	111		86	123.5	122.1	Xr	1.2	70
O-C(3)-O	126	112.6	111.5	Nd	1.0	142	C(X)-N(X)-C(X)	34	103.5 ^{min}	109	Xr	-0.4	64
O-C(8)=O	30	124.4	120.9	Xr	2.9	129			110.5	110		0.3	

Table 10. (continued)

Angle ^a	Mole- cule ^b	θ^c_{calcd}	θ^c_{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f	Angle ^a	Mole- cule ^b	θ^c_{calcd}	θ^c_{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f
C(6)-N(2)-C(6)	38	110.9	112.2	Mw	-1.2	108a	C(3)-N(8)-C(7)	83	124.8	123.4	Xr	1.1	75
			111.8	Ed	-0.8	108b	C(6)-N(8)-C(7)	58	121.3	121.0	Xr	0.3	120
	39	110.9	110.9	Mw	0.0	109		65	127.6	127.6	Xr	0.0	118a
			110.6	Ed	-0.3	108b				129.3	Xr	-1.3	118b
	56	108.6 ^{mbh}	108.2	Xr	0.4	112		66	121.1	119.6	Xr	1.3	117
		110.3	110.6		0.3		C(1)-N(8)-C(6)	66	121.4	121.7	Xr	-0.2	117
	57	110.3	109.8	Xr	0.5	35	C(6)-N(8)-C(6)	58	117.4	117.4	Xr	0.0	120
	91	111.3	110.0	Xr	1.1	43	C(6)-N(9)=C(10)	137	104.6	105.4	Xr	-0.8	110
	13	107.6	108.3	Xr	-0.6	81a		138	104.2	103.8	Xr	0.4	111
			108.4	Xr	-0.7	81b	C(6)=N(5)=C(6)	118	116.3	117.1	Xr	-0.7	41
	118	108.2	109.5	Xr	-1.2	41		120	116.8	116.9	Mw	0.0	105
	112	106.8	109.8	Mw	-2.7	104		136	114.6	115.2	Xr	-0.5	115
	115	108.1	110.1	Xr	-1.8	40		138	115.4 ^{β_1}	118.4	Xr	-2.5	111
	116	106.6	108.9	Xr	-2.1	72			112.6 ^{β_2}	113.0		-0.4	
	117	106.7	109.0	Xr	-2.1	83		140	106.0	106.1	Xr	0.1	90
	140	109.6	108.6	Xr	0.9	90		141	107.3	106.1	Xr	1.1	114
C(6)-N(2)-C(10)	137	106.3	107.2	Xr	-0.8	110	C(1)-N(12)=O	121	113.4	112.6	Mw	0.7	122
	138	106.2	106.5	Xr	-0.3	111	C(1)-N(13)=O	122	118.0	117.4	Mw	0.5	123
C(1)-N(8)-C(7)	47	122.2	121.4	Ed	0.7	116	C(6)-N(13)=O	123	118.6	118	Xr	0.5	124
	49	121.2	119.7	Ed	1.3	73a				117.8	Mw	0.7	139
			120.5	Xr	0.6	73b	O=N(13)=O	122	124.1	125.3	Mw	-1.0	123
	60	121.2	122.4	Xr	-1.0	77		123	122.8	124	Xr	-1.0	124
C(2)-N(8)-C(7)	62	122.6	121.3	Xr	1.1	76				124.4	Xr	-1.3	139
	63	122.5	122.7	Xr	-0.2	78	C(X)-O-C(X)	51	119.5	120.0	Ed	-0.4	127
	116	122.0	122.5	Xr	-0.4	72		55	120.1	120	Xr	0.1	42

Table 10. (continued)

Angle ^a	Mole- cule ^b	θ^c_{calcd}	θ^c_{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f	Angle ^a	Mole- cule ^b	θ^c_{calcd}	θ^c_{exptl}	Method ^d	Percent rel. error ^e	Ref. ^f
	56	122.1	119.0	Xr	2.6	112	C(3)-O-C(4)	127	109.7 ^{ϵ_1}	111.6	Nd	-1.7	100b
	57	122.7	119.3	Xr	2.8	35			117.3 ^{ϵ_2}	114.3		2.6	
	96	113.7	111.7	Mw	1.8	128	C(6)-O-C(6)	119	107.1	104.4	Xr	2.6	82
	97	114.1	111.4	Mw	2.4	130		111	104.7	106.6	Mw	-1.8	103a
	109	120.0	120.7	Ed	-0.6	98			106.2	106.2	Xr	-1.4	103b
	110	120.3	119.7	Ed	0.5	99		114	106.0	107.3	Xr	-1.2	39
	113	105.9	106.4	Ed		133a	C(1)-O-C(8)	29	117.1	114.8	Mw	2.0	125
			109.7					30	117.6	117.6	Xr	0.0	129
			106.4	Ed		133b	C(2)-O-C(8)	31	117.9	116.4	Xr	1.3	132
			110.6					34	118.2	115	Xr	2.8	64
C(3)-O-C(3)	126	114.0	113.8	Nd	0.2	142	C(3)-O-C(8)	73	120.3	119	Xr	1.1	65
	127	114.8	116.0	Nd	-1.0	100b		124	108.0	110.2	Xr	-2.0	68
								125	122.1	124.1	Xr	-1.6	69

^aSee Table 9 for the description of angle types. ^bSee Fig. 2. ^cUnit is in degree. Superscripts refer to the particular bond angles of a molecule in Fig. 2. Superscripts m, q, t refer to methyl, quaternary and tertiary, respectively. An asterisk(*) shows the averaged value. ^dSee footnote d in Table 9. ^eSee footnote e in Table 9. ^fSee footnote f in Table 9.

Table 11. Adiabatic rotational barrier heights

Molecule	V^a		ΔE^b		Molecule	V^a	
	Calcd	Exptl	Calcd	Exptl		Calcd	Exptl
HCO-OH ^d	10.1 ^e	10.9 ^{ee}	5.0	2.0 ^{ee}	CH ₃ -CH ₃	2.70	2.95 ^m
HCO-OCH ₃ ^d	9.3 ^e	10.0 ^{ff}	2.5	2.3 ^{ff}	CH ₃ -COOH ^o	0.59	0.48 ⁿ
CH ₃ CO-OCH ₃ ^d	10.5 ^e	10.3 ^{gg}	3.8	4.3 ^{gg}	CH ₃ -CHO ^o	1.09	1.16 ^p
CH ₃ CO-OC ₂ H ₅ ^d	10.6 ^e	8.8 ^{gg}	4.1	4.5 ^{gg}	(CH ₃) ₂ -CO ^o	0.74	0.78 ^q
CH ₂ CH-CHO ^f	5.2 ^e	5.0 ^{hh}	-1.9	-2.1 ^{hh}	CH ₃ -CHCH ₂ ^o	2.09	1.98 ^r
CH ₂ CH-CHCH ₂ ^f	2.2 ^e	2.6 ⁱⁱ	-2.6	-2.3 ⁱⁱ	(CH ₃) ₂ -CCH ₂ ^o	2.31	2.21 ^s
C ₂ H ₅ -C ₂ H ₅	1.3 ^z	3.4 ^{aa}	1.1 ^{cc}	1.0 ^{cc}	cis CH ₃ -CHCHCH ₃	0.06	0.73 ^t
	4.4 ^{bb}	~7 ^{aa}			trans CH ₃ -CHCHCH ₃	2.09	1.95 ^u
CH ₃ -OH ^g	0.95	1.06 ^h			C ₆ H ₅ -OH ^w	3.30	3.36 ^v
CH ₃ -OCHO ^g	2.68	1.19 ⁱ			H ₂ N-CHO ^w	14.6	10-12 ^x
CH ₃ -OCH ₃ ^g	1.48	2.72 ^j					18 ^y
H ₂ N-CH ₃ ^g	1.84	1.96 ^k			C ₆ H ₅ -C ₆ H ₅	4.1	1.1 ^{jj}
HN-(CH ₃) ₂ ^g	3.66	3.62 ^l			HO-OH ^{ll}	0.9 ^{mm}	1.1 ^c
						6.6 ⁿⁿ	7.0 ^c

^a Barrier height(kcal/mol). ^b Relative conformational energy $E_{trans} - E_{cis}$ (kcal/mol). ^c Reference 147t. ^d The trans and cis nomenclature applies to the relative orientations of the C=O and O-X groups(X=H,C). ^e Barrier height from cis to trans. ^f The trans and cis nomenclature applies to the relative orientations of the C=C and C=X groups(X=O,C). ^g The calculated and experimental conformations of methyl groups are always near staggered. ^h Reference 147a. ⁱ Reference 125. ^j Reference 147b. ^k Reference 107. ^l Reference 147c. ^m Reference 147d. ⁿ Reference 147e. ^o The calculated and experimental conformations of methyl groups are eclipsed with respect to the C=X bond(X=O,C). ^p Reference 53a. ^q Reference 54a. ^r Reference 147f. ^s Reference 147g. ^t Reference 147h. ^u Reference 147i. ^v Reference 135b. ^w The calculated and experimental geometries of the molecules are planar. ^x Reference 119a. ^y Reference 147j. ^z Barrier height from gauche to trans. ^{aa} Reference 147k. ^{bb} Barrier height from gauche to gauche. ^{cc} Relative conformational energy $E_{gauche} - E_{trans}$. ^{dd} Reference 147l. ^{ee} Reference 147m. ^{ff} Reference 147n. ^{gg} Reference 147o. ^{hh} Reference 147p. ⁱⁱ Reference 147q. ^{jj} Reference 147r. ^{kk} The dihedral angles at energy minima are 41.4°(calcd) and 42°(exptl). See Reference 80a. ^{ll} The dihedral angles at energy minima are 115.6°(calcd), and 116.0°(lower ground state) and 120°(upper ground state). See Reference 147s. ^{mm} trans Barrier height. ⁿⁿ cis Barrier height.

Table 12. Hydrogen bond energies

Donor	Acceptor	Hydrogen bond energy, O...O distance, Å ^o kcal/mol			
		Calcd ^a	Exptl ^b	Calcd	Exptl
HO-H...	O=CH	-3.72	-3.33 ^{a,c,d} -3.5 ^{a,c,e}	2.84	2.88 ^{c,d} 2.87 ^{c,e}
CH ₃ O-H...	O=CH	-3.89	-3.48 ^d	2.85	2.86 ^d
CH ₃ O-H...	O=C(CH ₃) ₂	-4.13	-3.6 ^f	2.85	
CH ₃ O-H...	O=CCH ₃ OC ₂ H ₅	-4.38	-2.5 ^f	2.86	
C ₂ H ₅ O-H...	O=CCH ₃ OC ₂ H ₅	-4.34	-2.4 ^f	2.85	
C ₂ H ₅ O-H...	O=C(CH ₃) ₂	-4.23	-3.4 ^f	2.85	
C ₆ H ₅ O-H...	O=CCH ₃ OCH ₃	-4.61	-4.5 ^f	2.90	
C ₆ H ₅ O-H...	O=CCH ₃ OC ₂ H ₅	-4.51	-5.75 ^f	2.88	
C ₆ H ₅ O-H...	O=C(CH ₃) ₂	-4.31	-4.8 ^f	2.90	
C ₆ H ₅ O-H...	O=	-4.49	-4.5 ^f	2.91	

^a The total energy at energy minimum minus the one at energy at infinite separation.

^b ΔH observed in solution. ^c ab initio S.C.F. calculation.

^d Reference 12h. ^e Reference 12c. ^f Reference 12a.

CAPTIONS FOR FIGURES

- Figure 1 Procedure for parametrization. In the figure, p and x stand for the parameters of the potential functions and the coordinate of atoms of a molecule, respectively. A total energy, E , is expressed as a function of p and x , and a minimization is carried out with respect to x . In the loops (1) through (4) are shown the various kinds of experimental data used for parametrization of each energy component together with the parameters concerned in each loop, and testing of the parameters of E^{nb} and E^{el} is also shown.
- Figure 2 Molecules used for intramolecular studies. Molecules are listed which were used for parametrization and testing of the intramolecular interaction potential functions. The letters b , a , o , and t appearing to the right side of the molecules refer to the molecules, which were used for parametrization of these intramolecular terms E^b , E^{ang} , E^{op} , and E^{tor} , respectively. Some molecules are used which are the part of large molecules, and the methyl groups (Me^*) are substituted where the truncations of the bonds are done. The alphabetic and Greek letters with and without the subscripts are used to specify the bonds and angles, respectively and are referred to in Tables 2 and 3.
- Figure 3 Molecules used for crystal packing calculations. 18 molecules are listed, which were used for testing the parameters of E^{nb} and E^{el} .

Figure 1.

Figure 2.

Figure 2. (continued)

Figure 2.(continued)

Figure 2. (continued)

Figure 2.(continued)

Figure 2.(continued)

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Figure 2.(continued)

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Figure 2.(continued)

Figure 2.(continued)

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Figure 3.

1 $n\text{-C}_5\text{H}_{12}$ 2 $n\text{-C}_6\text{H}_{14}$ 3 $n\text{-C}_8\text{H}_{18}$ 5 $\text{H}_2\text{C}=\text{CH}_2$

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II. APPLICATION OF EMPIRICAL POTENTIAL FUNCTIONS TO THE
STUDIES OF PHOTOREACTION CENTER CHLOROPHYLL A DIMER.

Chapter II

1. Introduction

It is well known¹ that chlorophyll a (Chl a) (Fig. 1) plays an essential role in green plant photosynthesis. Chl a functions in at least three important capacities: (1) as an antenna pigment which absorbs light energy from the incident sunlight, (2) as a reaction center pigment which acts as a phototrap for excitation transferred from the antenna pigments, and (3) as a primary constituent in the light-induced electron transfer process. The antenna pigment consists of a large number of Chl a molecules which absorb visible light in the 678 nm region, while the reaction center contains a small number of Chl a molecules, surrounded by protein, which absorb around 700 nm and are called P700.

Much work has been done to understand the structural chemistry of P700 both in in vivo photosynthetic systems and in in vitro chemical model systems. P700 was identified first by Kok² who observed that bleaching (decrease in the intensity of light absorption) occurs at ~700 nm during active photosynthesis, and that the bleaching is reversed in the dark. The photobleaching is found to be an oxidative process³ in which an electron is ejected from P700, thereby creating a radical cation species $P700^{\cdot+}$. This species can be detected by electron paramagnetic resonance (EPR)⁴ spectroscopy, and has a free electron g-value of 2.0025 and a signal width of 7 gauss. The signal width of $P700^{\cdot+}$ was reduced relative to that of the monomeric Chl a cation radical in vitro

by a factor of about $1/\sqrt{2}$. This provides evidence which suggests that P700 is actually a pair of Chl a molecules, the so-called "special-pair" Chl (Chl_{sp}) dimers, since theory⁴ predicts that the signal should be narrowed by a factor of approximately $1/\sqrt{N}$ when an unpaired electron is delocalized equally over N equivalent Chl a molecules. Additional support for the participation of Chl a dimer in P700 has been provided by electron nuclear double resonance (ENDOR)⁵ spectroscopy.

2. Models for P700 Special-Pair Chl a Dimers

Essentially four different models have been proposed for P700. All have two Chl a molecules with their macrocyclic planes arranged in a parallel fashion, but they differ in the details of the relative orientation of the Chl a molecules, the distance between the macrocycles, and the functional groups (C=O groups) and nucleophiles used to "link" the two chlorophylls.

The first model (Model I) was proposed by the Argonne group⁶ and is shown in Figure 2. In this model a single water molecule is coordinated to the Mg atom of one Chl a and simultaneously hydrogen bonded to both the keto C=O and carbomethoxy C=O groups of the other Chl a molecules. A later modification of this model was developed (Model II) and is shown in Figure 3. This model was derived from the X-ray crystal structure of ethyl chlorophyllide a dihydrate,⁷ and involves two water molecules linking each pair of Chl molecules. Alternatively, a model (Model III) which possesses C_2 symmetry was proposed by Fong,⁸ and is shown in Figure 4. This model is distinct from the previous two models in that only the carbomethoxy C=O groups are engaged in hydrogen bonding and the

spacing between the macrocycle planes is $\sim 6 \text{ \AA}$, a distance substantially greater than the van der Waals contact distance of $\sim 3.5 \text{ \AA}$. A second C_2 model (Model IV) was proposed by Boxer and Closs⁹ based on their studies of a covalently linked pyrochlorophyllide a dimer, and by Shipman et al.¹⁰ based on low temperature visible and IR spectroscopic measurement. The structure is depicted in Figure 5. Later studies by Wasielewski et al.¹¹ on a covalently linked Chl a dimer further supported the structural conclusions drawn by Boxer and Closs⁹ and Shipman et al.¹⁰ Their model differs from the previous three models in that only the ring V keto C=O groups are involved in hydrogen bonds and the nucleophiles used to link the two Chl's need not be water molecules but can be any type of bifunctional ligand such as methanol.

Although these models are useful for qualitative analysis and interpretation of experimental data, quantitative information on the structure and stability of the various models has yet to be given. Quantum mechanical approaches to the search for likely minimum energy structures are obviously not applicable here due to the size of the system. However, empirical potential functions, which have been used quite successfully to study the structure and dynamics of proteins,¹² can be used efficiently. Therefore, we have developed an empirical potential function (EPF) to study the structure of large molecules, and have applied it to the study of Chl_{sp} and related dimer systems. Although much is now known about the role and importance of Chl_{sp} in photosynthetic energy conversion, little is known about its detailed geometric structure, and such information is essential if the mechanism of photosynthetic energy production is to be fully understood.

3. Description of the Empirical Potential Function

The form of the potential function that is used is given by

$$E = E^b + E^{ang} + E^{tor} + E^{op} + E^{nb} + E^{hb} + E^{el}, \quad (1)$$

where E^b is a bond deformation energy, E^{ang} is an angle deformation energy, E^{tor} is a torsional strain energy, E^{op} is an out-of-plane deformation energy (for bending at sp^2 hybridized C atom), E^{nb} is a non-bonded interaction energy, E^{hb} is a hydrogen bond energy, and E^{el} is an electrostatic interaction energy. A formula for each energy component and details of the parameter development will be given elsewhere.¹³ The parameters for these potential terms were developed from experimental data on bond lengths and angles, electric dipole moments, torsional barrier heights, and hydrogen bond energies for small molecules. Tests of the reliability of the non-bonded parameters for studying intermolecular interactions were provided by calculations of the unit cell constants and lattice binding energies for a number of molecular crystals. The accuracy of the predicted geometric parameters is ~ 0.01 Å for bond lengths and $\sim 2^\circ$ for bond angles, $\sim 3^\circ$ for torsional angles and ~ 0.05 Å for non-bonded distances. In the studies of chlorophyll and related molecules, parameters involving Mg atom are required. In our studies three types of potential energy terms were used: E^{nb} , E^{el} and E^{op} . Determination of the relevant parameters is given in Appendix 1.

4. EPF Calculations of Chl Dimer Structure

The total energy described by eq. (1) was minimized with respect to the $3N$ Cartesian coordinates of the dimer, where N is the number of atoms (N is 182 for the largest system studied here). Minimization of the various dimer structures is carried out by a modified quasi-Newton method (i.e., Davidon-Fletcher-Powell algorithm)¹⁴ using analytical Cartesian derivatives of the potential function.

In the optimizations, ethyl chlorophyllide a (Et-Chl a) and methyl pyrochlorophyllide a (Me-PChl a) were used rather than Chl a and PChl a. Justification for this modification is based on the NMR studies¹⁵ of Chl a in solution, which show that the phytyl group undergoes free movement in both dimeric and monomeric species. Thus, removal of the phytyl group is not expected to alter seriously the structural conclusions reached in the present study.

Table I summarizes the interaction (i.e., binding) energies (ΔE) of the various dimers, together with the contributions to ΔE due to non-bonding interactions (ΔE^{nb}), electrostatic interactions (ΔE^{el}), and hydrogen bonding (E^{hb}).

Model I: (Chl.H₂O.Chl)

This model has a substantial binding energy (-35.1 kcal/mol) despite participation of only a single water molecule. As in Models I-IVa (see Table I), the main contribution to the stability comes from non-bonded interactions. The planes of the macrocycles, defined by the plane passing through atoms N1, N2 and N3, are found to lie at an angle of $\sim 27^\circ$ with respect to each other, with a spacing of ~ 4.6 Å between

ring V of the upper Chl and ring I of the lower Chl. A starting geometry and a final geometry after minimization are depicted in Figures 6a and 6b, respectively.

The non-parallel arrangement and spacing beyond the van der Waals distance (3.4-3.6 Å) are due to a combination of two effects: (1) the bulky carbomethoxy group of the upper Chl is placed between the macrocycles, thus prohibiting the π - π contact of the rings; (2) simultaneous hydrogen bonding by a single H₂O to the two C=O groups of the upper Chl which prohibits the formation of optimum angles for hydrogen bond formation (the H-O..O angle at the keto C=O group was found to be $\sim 24^\circ$ as opposed to an optimum linear hydrogen bond angle of 0°). The two ester side chains at ring IV are nearly parallel to each other and separated by ~ 8.5 Å, and thus the interaction of these chains has no effect on the formation of the dimer in this model.

Model II: (Chl.H₂O)₂

This model, based on the X-ray crystal structure of ethyl chlorophyllide a dihydrate (Chl.2H₂O),⁸ is found to be fairly stable (binding energy of -39.6 kcal/mol). The two H₂O molecules are involved in three hydrogen bonds, which have a significant effect on both the geometry and energy of dimer formation. The H-O..O angle for each of the three hydrogen bonds is $\sim 10^\circ$, and is much closer to linearity than that found in Model I ($\sim 24^\circ$). The O..O distances are 2.8 (H₂O..keto), 2.9 (H₂O..H₂O) and 2.9 Å (H₂O..ester), and are comparable to the experimental values of 2.7, 2.8 and 3.0 Å, respectively, found in the Chl dihydrate.⁷ The two macrocycles are almost parallel to each other, and the spacing is found

to be ~ 4 Å. As is indicated by the Mg..Mg distance of ~ 9 Å, the two Chl molecules are sufficiently separated so that no appreciable interactions due to steric crowdings of the side chains occur. A starting geometry was taken from the X-ray structure of Chl. $2H_2O$ (see Fig. 3),⁷ and the final geometry obtained after energy minimization was essentially unchanged from the initial geometry.

Model III: (Chl. $2H_2O$)₂

Unlike the previous two models, this model employs only the carbomethoxy C=O groups in the hydrogen bonds. The keto C=O groups are not utilized at all. The hydrogen bond angle H-O..O and the O..O distance are found to be $\sim 24^\circ$ and 2.69 Å, respectively. Due to the presence of two bulky carbomethoxy groups between the macrocycles, it was expected that this model would be the least stable of all. As is seen in Table I, the binding energy is found to be -39.9 kcal/mol, and is approximately as stable as Model II. The two macrocycles are found to be almost parallel to each other with spacing of ~ 6 Å. Despite this distance, which is much larger than the van der Waals distance of ~ 3.5 Å, the non-bonded interaction energy between the macrocycles is substantial (-19.6 kcal/mol) and is attributed to the face-to-face arrangement of the two macrocycles (see the Mg..Mg distance of 6.2 Å in Table I). This is contrary to Model II where the overlap of the macrocycles is the least of all the models as is indicated in the Mg..Mg distance (9.0 Å), and therefore the non-bonded interaction energy (-16.8 kcal/mol) between the two macrocycles is least, as would be expected.

A starting geometry with a spacing of 6.0 Å between the two parallel

macrocycles as was proposed by Fong⁸ was used (see Fig. 7a), and the final geometry after energy minimization is given in Figure 7b. Although the final geometry is found to be only slightly different from the initial one, the energies of these geometries are quite different, i.e., -39.9 and -0.6 kcal/mol, respectively. Since the minimization using the DPF algorithm stopped at the very early stage (after the second iteration) with an interaction energy of only -6.9 kcal/mol, it was expected that the minimization had reached a local minimum. Therefore, a further minimization using the pattern-search method¹⁶ was pursued to get a more stable minimum using the local minimum as a starting point. The interactions energy of -39.9 kcal/mol was thus obtained after this additional minimization process.

Model IVa: (Chl.H₂O)₂

Unlike the previous three models, the nucleophile used in Model IV to link the two Chl molecules can be any bifunctional hydrogen-bonding ligand RXH,¹⁰ where X is O, NH, or S, and R is H or alkyl. In our studies of Model IV, two kinds of nucleophiles (H₂O and CH₃OH) were used (e.g., see Models IVa and IVl of Table I).

Model IVa, which employed water as the bifunctional ligand, has a binding energy of -49.6 kcal/mol and this is the most stable structure of Models I-IVa. The dimer structure is given in Figures 8a and 8b. The planes of macrocycles are at an angle of $\sim 10^\circ$ to each other with spacing of ~ 3.6 Å between the rings III and V of both molecules, and the overall structure has approximate C₂ symmetry. The hydrogen bond angle H-O...O at ring V is $\sim 7^\circ$, and the O...O distance is ~ 2.8 Å. Two

different starting geometries, both of which have spacing of 4.0 Å between the two parallel macrocycles but differ in the Mg..Mg distance (i.e., 7.7 and 8.6 Å), gave essentially the same binding energy and structure, as is shown in Figure 8. Figure 8b also shows that a fairly large amount of space can be occupied by the nucleophile, thus allowing the bulkier nucleophiles than the H₂O to participate in linking the two macrocycles. In Models I and III this was not possible.

The above comparison clearly suggests that Model IVa is the most favorable both energetically and geometrically, although the other models have substantial binding energies. In comparing these four models a few additional comments are appropriate:

(i) In Models II and III, the Mg is displaced 0.4 Å on the carbomethoxy side of the macrocycle as found in X-ray crystal structure for ethyl chlorophyllide a 2H₂O,⁷ while in Models I and IVa, the Mg is located on the side opposite the carbomethoxy group. There seems to be no compelling reason why the Mg should not be displaced with almost equal probability to either side of the macrocycle. A preliminary analysis¹⁷ of the X-ray data of bacteriochlorophyll a protein from Prostheochloris aesturarii indicates that Mg may appear on either side of the macrocycles. Our calculation of ethyl chlorophyllide a with Mg on the same and opposite sides of the carbomethoxy group shows that the latter case is more stable by ~2 kcal/mol.

(ii) The C=O..Mg interaction seems to have a significant effect on the dimer formation in all of the four models. The O..Mg distance ranges from 4.1-4.8 Å and contributes an electrostatic interaction energy of -14 to about -16 kcal/mol.

(iii) Table I shows that, in all of the four models, the binding energy is attributed solely to the intermolecular interactions and not to the intramolecular interactions. This, of course, does not necessarily mean that the geometry of the molecule does not undergo any change in going from monomeric to dimeric form. Although the changes in bond lengths and angles are found to be very small, i.e., $\sim 0.002 \text{ \AA}$ and $\sim 0.3^\circ$, respectively, the dihedral angles of the side chains undergo appreciable changes. In a relatively uncrowded system like Model IVa, for example, the largest changes found at the carbomethoxy and ring IV ester are $\sim 4^\circ$ (around a bond O_3-C_{10a}) and $\sim 8^\circ$ (around a bond $C_{7b}-C_{7c}$), respectively.

(iv) As pointed out earlier, besides the hydrogen bond the main contribution of water to the stability of dimeric Chl species is due to electrostatic rather than non-bonded interactions. On the other hand, the electrostatic interaction energy between the nacrocylic rings is very small, i.e., 0.1 (Model I), 0.8 (Model II), 3.9 (Model III), and -1.2 kcal/mol (Model IVa).

The results presented in the previous section indicate that, of the models examined, Model IV is the most probable model for P700. Low-temperature IR studies by Cotton et al.¹⁸ provide additional support for this model, since they show that, for the Chl a-ethanol adduct in toluene, the ring V keto carbonyl rather than the ester carbonyl of the carbomethoxy group is hydrogen-bonded to ethanol.

To characterize Model IV further, a number of additional studies were carried out. These studies included an evaluation of the shape of the potential energy surface around the calculated energy minimum, the

effect of the presence of the carbomethoxy group and of different bifunctional ligands on dimer formation. The various types of systems chosen for study are listed in Table I.

A. Potential energy surface of Chl..Chl interaction

As we found earlier in the study of Models I-IVa, the binding energy of the dimer is almost entirely attributed to the intermolecular interaction. Therefore, only non-bonded and electrostatic interactions are employed in a study of the potential energy surface generated by the interaction of two rigid (i.e., unrelaxed) Chl molecules. As shown in Figure 9a, the two macrocycles are arranged in a parallel fashion with a fixed spacing of 3.6 Å, and the interaction energy of the Chl.Chl dimer was calculated as a function of the displacements of the Mg atom of the lower Chl molecule along the x and y axes relative to the Mg atom of the upper Chl molecule. A spacing of 3.6 Å was chosen after examining the effect of variation in the spacing on the interaction energy, and the maximum interaction energy was obtained at a spacing of ~3.6 Å; i.e., distances less than 3.6 Å produced substantial repulsive energy which destabilized the complex, and distances greater than 3.6 Å had weaker attractive forces and thus were also less stable. The result of this calculation is shown in Figure 9b as a contour map, and the energy minimum is found at point 1 of Figure 9b. Minimum points found by adiabatically relaxed minimizations of the various other systems (see points ② - ⑥ and ②' - ⑤' in Figure 9b) related to Model IV, and the minimum point ①' found by rigid body minimization of the PChl..PChl dimer are also shown. In all of these adiabatic studies, the optimum

spacing between the macrocycles is found to be ~ 3.6 Å.

Figure 7 depicts the minimum energy structure of the covalently linked $(\text{Chl.H}_2\text{O})_2^{\text{COV}}$ dimer (see also point ④ of Figure 9b). Comparing this figure with that of the non-covalently linked $(\text{Chl.H}_2\text{O})_2$ dimer (see also point ③ of Figure 9b) shows quite clearly that structurally and energetically the two systems are very similar, the main difference being the orientation of the ester side chains of ring IV.

Although the potential energy surface in Figure 9b is obtained by rigid body minimization, an adiabatically relaxed minimization is not expected to cause a significant change in the overall shape of the surface, although possible shifts in minima (see the shifts ① $\rightarrow$ ② and ①' $\rightarrow$ ②') occur as expected. The minimum points (② - ⑥ and ②' - ⑤') found in the various systems obtained by an adiabatically relaxed minimization are essentially in the same region, considering the size of the molecule and the number of degrees-of-freedom (over 500) used in the minimization. Convergence to approximately the same region suggests that the minima shown in Figure 9b represent structurally important energy minima.

Due to the large number of degrees of freedom involved, it is expected that there exist many local minima around the true minimum. Since energy minimization schemes cannot, in general, be made to avoid false minima entirely, the chances of reaching local minima will be especially greater when the minimization is begun at a point far from an energy minimum point which represents a particular stable structure.

As an example, in Model IVa we have chosen an initial point far from the energy minima shown in Figure 9b (i.e., $x = \sim -8.0$, $y = \sim 0.0$,

$z = \sim 3.6$), where the two macrocycles are arranged in a parallel fashion with a spacing of $4.0 \text{ \AA}$ (i.e., $z = -4.0 \text{ \AA}$), and x and y are chosen to be -6.0 and $0.0 \text{ \AA}$, respectively. In this initial geometry the interaction between the two molecules is highly repulsive, as can be seen from Figure 9b, and the distance between the two ring IV ester side chains is too close (the distance between the two carbonyl oxygens is less than the van der Waals distance of $\sim 2.8 \text{ \AA}$). Minimization reached a local minimum with a binding energy of -41.0 kcal/mol , where x and y are found to be -7.2 and $0.0 \text{ \AA}$, respectively. At this minimum the two macrocycles make an angle of $\sim 24^\circ$, and the separation of rings (rings III and V) ranges from 4.5 to $5.0 \text{ \AA}$. Therefore, the starting geometries used in the adiabatically relaxed minimizations of Model IV (Model IVa-Model IVe) were carefully chosen, and geometries having highly repulsive energy in the initial stages of minimization were discarded.

From an examination of Figure 9b and Table I, several observations can be made, as will be discussed in the following sections.

B. Comparison of rigid body and adiabatically relaxed minimization of $(\text{Chl})_2$

In the rigid body minimization (RBM), the minimum energy was found to be -20.5 kcal/mol with contributions of -19.6 kcal/mol from the non-bonded and -0.9 kcal/mol from the electrostatic interactions energies, respectively. In the adiabatically relaxed minimization (ADM), the total binding energy is -26.9 kcal/mol with -24.9 and -2.3 kcal/mol representing the contributions from the non-bonded and electrostatic interaction energies, respectively. The minimum energy point found in

the ADM (i.e., point ②) is shifted in the x-direction (see Fig. 9b) by ~ 1.0 Å from that found in the RBM (i.e., point ①), so as to allow the more π - π overlap of the two macrocycles. This shift is attributed to the fact that, in the ADM, the ester side chains of rings IV and V are allowed to move and this relaxation reduces the repulsive interactions experienced by the groups in the RBM. That such relaxation effects are important is seen from the fact that changes in the dihedral angles in these groups in going from monomeric to dimeric form are as much as $\sim 5^\circ$ and $\sim 10^\circ$ for the ring V carbomethoxy group and the ring IV ester side chain, respectively. Similar observations, i.e., the change in binding energy (7.4 kcal/mol), the shift (~ 1.0 Å) of the minimum energy point, and the change in dihedral angles (as much as $\sim 9^\circ$) of the ring V ester group, are found in the $(\text{PChl})_2$ system.

C. Effect of H_2O on dimer formation

The results of calculations on various Model Systems given in Table I (i.e., MS8-MS11) summarize the energy minimization studies carried out on the $(\text{Chl})_2$ and $(\text{PChl})_2$ dimers, as well as the covalently linked dimers of the respective species, $(\text{Chl})_2^{\text{COV}}$ and $(\text{PChl})_2^{\text{COV}}$, with and without the presence of H_2O . As is seen from the table, the presence of H_2O provides substantial stability ($-22\sim-25$ kcal/mol) to the complex, thus considerably enhancing dimer formation. Most of the stability is, however, due to the electrostatic interaction and hydrogen bonding, and the effect of the non-bonded interaction is small. The results of calculations on $(\text{Chl})_2$ (i.e., MS6) and $(\text{PChl})_2$ (i.e., MS7) show that, without H_2O , $(\text{Chl})_2$ and $(\text{PChl})_2$ form fairly stable dimers with binding

energies of -26.9 and -23.3 kcal/mol, respectively. Although most ($\sim 90\%$) of the stability is due to the non-bonded interaction, the contribution ($\sim 10\%$) of the electrostatic interaction is not negligible. The non-bonded interaction between the macrocycles plays an important role to the stability of the dimer. Our independent study of magnesium porphine dimer, where two porphine rings are arranged in a parallel fashion with spacing of ~ 3.5 Å, shows that the contribution of the non-bonded interaction energy to the binding energy (~ -23 kcal/mol) is ~ -24 kcal/mol, which is comparable to those, -24.9 and -21.4 kcal/mol, found in $(\text{Chl})_2$ and $(\text{PChl})_2$, respectively.

As we can see in the results of calculations on $(\text{Chl} \cdot \text{H}_2\text{O})_2$ (i.e., MS4) and $(\text{Chl})_2$ (i.e., SM6), the presence of H_2O has no effect on the interplanar distance between the macrocycles, but slightly inhibits the parallel movement of the macrocycles, reducing the overlap of rings III and IV of both molecules. This is indicated by the Mg..Mg distance (i.e., 8.6 and 7.9 Å with and without H_2O , respectively), and is due to the geometrical restriction imposed by hydrogen bonding of keto $\text{C}=\text{O}$ and H_2O .

D. Other remarks

After synthesis of covalently linked pyrochlorophyll a dimer $(\text{PChl } \underline{\text{a}})_2^{\text{cov}}$ by Boxer and Closs⁹ as a model of P700, synthesis of a covalently linked chlorophyll a dimer $(\text{Chl } \underline{\text{a}})_2^{\text{cov}}$ was carried out by Wasielewski et al.¹¹ in order to test, among other things, the effect of possible steric effects due to the carbomethoxy group at ring IV which is absent in $(\text{PChl } \underline{\text{a}})_2^{\text{cov}}$. However, in our studies of the various models,

$(\text{Chl} \cdot \text{H}_2\text{O})_2$, $(\text{PChl} \cdot \text{H}_2\text{O})_2$, $(\text{Chl})_2$, $(\text{PChl})_2$, $(\text{Chl} \cdot \text{H}_2\text{O})_2^{\text{cov}}$, $(\text{PChl} \cdot \text{H}_2\text{O})_2^{\text{cov}}$, $(\text{Chl})_2^{\text{cov}}$, and $(\text{PChl})_2^{\text{cov}}$, it was found that the carbomethoxy group has no significant effect on the formation of the dimer. Specifically, the Mg..Mg distance and the interplanar distance between the macrocyclic rings, as well as the angle made by these rings, are not affected appreciably by the presence of the carbomethoxy group (cf. Table I). Thus, this result indicates that the carbomethoxy-less PChl could also be a good model to study P700.

Although replacement of H_2O by the bulkier ligand CH_3OH produced a dimeric species that was 2.3 kcal/mol more stable than that obtained with H_2O , no appreciable changes in the dimer structure are found when comparing the structures of the two dimers. It is not likely that the replacement of the CH_3 - group by a bulkier alkyl group would cause any geometrical changes in the dimer, since, as is seen in Figure 8b, the region of the alkyl side is sufficiently open so as not to present any steric restrictions.

5. Summary

In the present study by an empirical potential function, it is shown that Model IV is the most likely model for the P700 chlorophyll dimer of all the models examined, from the energetical and geometrical points of view. Besides hydrogen bonding, the electrostatic interaction of cross-linking nucleophiles with chlorophyll molecules plays an energetically important role in the dimer formation. It is also found that the involvement of the carbomethoxy $\text{C}=\text{O}$ group in the hydrogen bonding with a cross-linking nucleophile causes a geometrically unfavorable

arrangement of the two chlorophyll molecules and thus reduces the stability of the dimer.

The open space around the nucleophile (see Figs. 8 and 10) and the relatively flat shape around the energy minimum, as well as the fairly soft interaction energy surface along the negative x-direction shown in Figure 9b, permit entry of rather large nucleophilic groups. This could allow a greater possibility of direct interaction of Chl with surrounding proteins, since the nucleophiles characteristically present in the side chains of the protein (e.g., -OH, -NH₂, -SH etc.) could be used to form the dimer.

Although the two macrocycles of the most stable structure for P700 were found to be approximately parallel, it is interesting to see the stability of a dimer where the two molecules are held by the keto C=O..Mg interaction and the two macrocycles are not parallel. In Figures 11a and 11b are given a minimum energy structure of (Chl)₂ with the Mg..O(=C) distance of 2.9 Å and the angle of 21° between the two macrocycles. The interaction energy was found to be -20.4 kcal/mol and is less stable than the one (-26.9 kcal/mol) found in the dimer where two macrocycles are arranged approximately in parallel (i.e., ~8°) (see the result of MS6 in Table I). An initial geometry of this adiabatically relaxed minimization was created as was proposed by Katz.¹⁹⁾

It was pointed out that Model IV is most consistent with the in vivo and in vitro experimental data, and our study provides further evidence of support for Model IV as a P700 chlorophyll dimer at the photoreaction center of green plants.

Table I. Interaction Energies of P700 Models.

Model System (MS) ^a			Contribution to ΔE^b (kcal/mol)					
MS	Model	Reference of MS	ΔE	ΔE^{nb}	ΔE^{el}	E^{hb}	R^c (Å)	Δd^d (Å)
1	I (Chl.H ₂ O.Chl)	2Chl+H ₂ O	-35.1(-20.3)	-23.6(-22.5)	-7.9(0.1)	-5.8	7.5	-4.6
2	II (Chl.H ₂ O) ₂	2(Chl+H ₂ O)	-39.6(-16.5)	-18.8(-16.8)	-10.2(0.8)	-10.1	9.0	-4.0
3	III (Chl.H ₂ O) ₂	2(Chl+H ₂ O)	-39.9(-12.8)	-21.9(-19.6)	-11.1(3.8)	-7.6	6.2	-6.1
4	IVa (Chl.H ₂ O) ₂	2(Chl+H ₂ O)	-49.6(-24.1)	-25.6(-23.2)	-17.5(-1.2)	-6.9	8.6	-3.6
5	IVa' (PChl.H ₂ O) ₂	2(PChl+H ₂ O)	-48.4	-24.2	-18.5	-6.9	8.2	-3.6
6	IVb (Chl) ₂	2Chl	-26.9	-24.9	-2.3		7.9	-3.6
7	IVb' (PChl) ₂	2PChl	-23.3	-21.4	-2.8		8.0	-3.6
8	IVc (Chl.H ₂ O) ₂ ^{cov}	(Chl) ₂ ^{cov}	-22.2	-2.6	-14.4	-6.5	8.7	-3.6
9	IVc' (PChl.H ₂ O) ₂ ^{cov}	(PChl) ₂ ^{cov}	-24.6	-3.7	-15.4	-6.6	8.4	-3.6
10	IVa (Chl.H ₂ O) ₂	(Chl) ₂	-22.6	-0.7	-15.3	-6.9	8.6	-3.6
11	IVa' (PChl.H ₂ O) ₂	(PChl) ₂	-25.1	-2.8	-15.5	-6.9	8.2	-3.6
12	IVd (Chl.MeOH) ₂	2(Chl+MeOH)	-51.9	-32.4	-14.4	-6.3	8.5	-3.6
13	IVe (PChl) ₂ ^{cov}	(PChl) ₂ ^{extcov}	-26.3	-17.1	-3.5		8.3	-3.6

^a Chl and PChl refer to ethyl chlorophyllide a and methyl pyrochlorophyllide a, respectively.

The symbol cov applies to both covalently-linked Chl a and PChl a dimers,

and the symbol extcov refers to a conformational isomer of the covalently linked dimer with extended form. ^b ΔE^{nb} , ΔE^{el} , and E^{hb} are the contributions of the nonbonded interaction, electrostatic interaction, and hydrogen bond energies, respectively, to the total interaction energy ΔE . The number inside parenthesis shows the interaction energy between the two Chl molecules in the absence of water. ^c R is the distance between two Mg atoms. ^d Δd is the approximate spacing between the two macrocycles.

CAPTIONS FOR FIGURES.

- Figure 1 Ethyl chlorophyllide a. In chlorophyll a the ethyl group at O_5 is replaced by an unsaturated aliphatic group $-C_{20}H_{39}$ (phytyl group). In pyrochlorophyll a, the ethyl group at O_5 is replaced by a phytyl group and the carbomethoxy group at C_{10} by H atom.
- Figures 2-5 Model I- Model IV. In the figures only ester groups are drawn for simplicity. In Fig. 5 the replacement of two R groups by $-CH_2-CH_2-$ gives covalently linked chlorophyll dimer.
- Figure 6a(6b) Initial(6a) and final(6b) geometries of Model I in adiabatically-relaxed minimization. In Fig. 6a, the molecule in the upper left is shifted by 6 Å to the left and 3.5 Å upward relative to the lower molecule. And the spacing between the two parallel macrocycles is 5 Å.
- Figure 7a(7b) Initial(7a) and final(7b) geometries of Model III in adiabatically-relaxed minimization.
- Figure 8a(8b) Minimum energy structure of $(Chl.H_2O)_2$ of Model IVa.
- Figure 9a Two ethyl chlorophyllide a (Chl) molecules are arranged in parallel fashion with interplanar distance of 3.6 Å. Interaction energy of two Chl's are calculated as a function of x and y, result of which is shown in Fig. 9b as a contour map.
- Figure 9b Interaction energy of Chl..Chl obtained by rigid body minimization is shown by a contour map, and the minimum energy is shown at point ①. Contour levels are given in kcal/mol and are in increments of 4 kcal/mol. The minimum energy points(②-⑥ and ②'-⑤') of various Chl and PChl dimers obtained by adiabatically-relaxed minimization are also shown together with a minimum energy point(①') of $(PChl)_2$ obtained by rigid body minimization.
- Figure 10a(10b) Minimum energy structure of $(Chl.H_2O)_2^{COV}$ of Model IVc.
- Figure 11a(11b) Minimum energy structure of $(Chl)_2$. This structure is less stable than the one, in which the two macrocycles arrange in parallel fashion(see text for details).

Figure 1.

Figure 2. Model I

Figure 4. Model III

Figure 3. Model II

Figure 5. Model IV

Figure 6a

Figure 6b

Figure 7a

Figure 7b

Figure 8a

Figure 8b

Figure 9b

Figure 9a

Figure 10a

Figure 10b

Figure 11a

Figure 11b

Appendix 1.

(i) Parameters for Mg atom in E^{nb} :

The potential function for nonbonded interactions between two atoms of the same kind is given by

$$E = ae^{-br} - c/r^6 \quad (2)$$

which has a minimum energy E_m at the separation of r_m . The parameters a , b , and c in eq. (2) for Mg..Mg interaction are derived from comparison with those¹³ for the H..H, C..C, N..N, and O..O nonbonded interactions.

Since the repulsion between the atoms becomes larger as the size of the atoms increases, a linear relationship was found between the van der Waals radius (r_{vw})²⁰ and the value¹³ of the parameter b in the atoms H, N, and O, and was used to derive the parameter b for the Mg atom. As found in the X-ray crystal structures of ethyl chlorophyllide a dihydrate⁷ and related molecules,²¹ the distance between Mg and the oxygen of the water is approximately 2.0 Å and is much shorter than the sum of the r_{vw} 's of the Mg(1.75 Å)²² and the O(1.4 Å) atoms. Therefore, the ionic radius²⁰ 0.65 Å of Mg²⁺ ion was used instead of the r_{vw} , and a value of 4.21 Å⁻¹ was obtained for the parameter b .

To derive the value of the parameter c , the relation

$$c = E_m / (6/r_m^7 b - 1/r_m^6) \quad (3)$$

was used, where a value -0.33 kcal/mol was obtained for E_m from a linear relationship found between the atomic number and E_m ¹³ in the atoms C, N, and O. A value 1.74 Å of r_m was obtained from the nearly linear relationship between r_{vw} and r_m ¹³ in the atoms H, O, and N. The value of the remaining parameter, a , was obtained from a relation

$$a = 6E_m e^{br_m} / r_m^7 b \quad (4)$$

A geometric mean value was taken for the parameters corresponding to

the interaction between the Mg atom and other atoms, and the parameters thus obtained are given in Table II.

(ii) Parameter for Mg atom in E^{el} :

A partial charge Q of 1.5 (in electronic unit) for Mg was calculated from a bond moment of N(pyrrole nitrogen)-Mg which was obtained from the dipole moment of magnesium porphine obtained from an ab initio SCF calculation.²³ A more detailed account of the procedure for obtaining partial charges from bond moments is given in reference 13.

(iii) Parameters for Mg atom in E^{op} :

Since the Mg atom is found to be 0.3-0.4 Å above the plane of four pyrrole nitrogens in the chlorophyll related molecules,^{7,21} the more generalized out-of-plane potential function in the following form was used.

$$E_{Mg}^{op} = f_{ijkMg}^{op} (d - d_0)^2 \quad (5)$$

where subscripts ijk refer to the pyrrole N atoms, d is the distance of Mg from the plane of atoms i,j,k , and the sum is taken over all the combinations of the three N atoms.

An equilibrium distance d_0 was set equal to 0.4 Å, and a value 100.0 kcal/mol Å² was chosen for the force constant f_{ijkMg}^{op} . The value of the force constant was chosen to be large enough to insure the out of plane distance of Mg atom would equal d_0 after the energy minimization, but not so large that E_{Mg}^{op} completely outweighs the other energy components at the start of minimization.

The only experimental data available for the test of parameters thus chosen for Mg atom is a distance (~ 2.0 Å) between Mg and the oxygen of the water found in the X-ray crystal structures of ethyl chlorophyllide a dihydrate⁷ and related molecules.²¹ Therefore, the energy minimization was carried out on magnesium porphine..water complex, where the oxygen of

the water was placed 3.0 Å above the Mg atom at the start of minimization, and the O...Mg distance was found to be 2.04 Å at the energy minimum(-8.1 kcal/mol).

Table II. Parameters for Mg atom in E^{nb}

Atom Pair	a(kcal/mol)	b(Å ⁻¹)	c(kcal Å ⁶ /mol)
H...Mg	3844.34	3.97	65.97
C...Mg	5922.96	3.62	176.99
N...Mg	11977.0	3.84	196.13
O...Mg	11977.0	3.87	196.13
Mg...Mg	2268.31	4.21	50.62

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