CHAPTER 5

5. THEORETICAL CALCULATIONS

5.1 Introduction to Molecular Modeling

The goal of structural chemistry is to derive accurate information of the three-dimensional geometries of molecules. X-ray diffraction of single crystals is a powerful method to determine molecular structures but it does not provide information about individual molecules in unusual environments.

In many cases the morphology of the crystal is not suitable and does not lend itself to X-ray analysis. For many compounds, crystals suitable for X-ray analysis are difficult or impossible to prepare; therefore detailed structural information of these compounds remains unknown. Many of these compounds have been subjected to detailed analysis and the results have served to establish many theoretical concepts in physical chemistry. X-ray analysis of single crystals can be costly and time-consuming. Specialized equipment is involved and the theoretical aspects of X-ray diffraction can be difficult to comprehend. A possible solution to these problems is to extend structural information, already available from X-ray diffractometry, to new structures. Molecular Modeling is a way to address this problem.

Methods used to calculate three-dimensional molecular structures are called Molecular Modeling. Two main approaches are used to calculate molecular structures. One approach involves quantum mechanical calculations and the other, molecular mechanical calculations. Quantum mechanical calculations may require large computer resources and the results may be difficult to interpret. Quantum mechanics describes molecules in terms of interactions among nuclei and electrons, and molecular geometry in terms of minimum energy arrangements of nuclei. All the quantum mechanical methods can ultimately be traced back to the Schrödinger equation[1]. For the special case of a hydrogen atom (a single particle in three dimensions), the Schrödinger equation may be solved exactly. Unfortunately, the multiple electron Schrödinger equation cannot be solved exactly even for the simplest multiple electron system. Approximations need to be introduced to provide practical methods to solve the equation. Quantum mechanics is used to establish equilibrium geometries and conformations and also to supply quantitative thermo chemical and kinetic data[1,2].

Molecular mechanical calculations are simpler and the resulting structural parameters may be more reliable than those obtained from quantum mechanical calculations. No one method of calculation is ideal for all applications. Great effort has been directed at finding suitable methods for different applications. Molecular mechanical methods may be applied to molecules containing 1000 or more atoms. Molecular modeling is generally applied to classical coordination complexes of transition metals and metal ions in states of moderate oxidation as well as to organic compounds.

Chemists believe that molecular properties like thermodynamic, kinetic and electronic properties are directly related to molecular structure[3]. Molecular mechanical calculations are now routinely employed by chemists to establish molecular equilibrium geometries and conformations. Calculations are being used not only to interpret experimental data, but also to supplement limited data or even replace it entirely. The success of any particular model firstly depends on its ability to consistently reproduce experimental data.

The basic principle behind molecular mechanics is the high degree of transferability of geometrical parameters from one molecule to another, as well as the predictable dependence of the parameters on atomic hybridization.

There are numerous methods available to compute molecular structures, but Molecular Mechanics is an approach that can optimize structures with high accuracy and is not as costly in terms of computer resources.

Molecular Mechanics makes use of the bond concept. This appeal to traditional chemist's idea that a molecule is a sum of bonded atoms and that molecular properties can often be written as the sum of contributions from each bond. The chemical bond between a pair of atoms is a function of the electron density distribution between atoms. In Molecular Mechanics this function is quantified in terms of the two atom types, which usually also define the bond order. Given atom types and bond orders imply a specific equilibrium (ideal) bond distance and a specific force is needed to distort this bond. Steric effects do not affect the bond order.

Molecular Mechanical calculations use the equations of classical mechanics to describe the potential energy surfaces and physical properties of molecules. A molecule is described as a collection of atoms held together by harmonic (elastic) forces. This description is called a force field. One component of a force field is the energy arising from compression and stretching of a bond. This component is often approximated as a harmonic oscillator and can be calculated using Hooke's law. The bond between two atoms is analogous to a spring connecting two masses. Using this analogy, Equation 5.1 gives the potential energy , V_{spring}, of the system as two masses joined by a spring and the force constant of the spring, K_r.

$$V_{spring} = \frac{1}{2} K_r (r-r_0)^2 \qquad \textbf{Equation 5. 1}$$

The equilibrium and the displaced distances of the atoms in a bond are r_0 and r. Both K_r and r_0 are constants for a specific pair of atoms connected by a certain spring. K_r and r_0 are force field parameters. The potential energy of a molecular system in a force field is the sum of individual components of the potential, such as bond distance, bond angle and Van der Waals potentials and coulombic interactions. The energies of the individual bonding components (bond distances, bond angles, dihedral angles) are functions of the deviation of a molecule from a hypothetical compound that has bonded interactions at minimum values.

Geometry optimizations find the coordinates of a molecular structure that represent a potential energy minimum. The absolute energy of a molecule in a molecular mechanical calculation has no intrinsic meaning. E_{Total} values are useful only for comparisons between molecules in the same chemical environment. The relative energies relate to the relative thermodynamic stabilities i.e. the lower the energy, the more stable the compound.

Molecular mechanics cannot describe bond formation, bond breaking or systems in which electronic delocalization or molecular orbital interactions play a major role in determining geometry or properties[4].

The aim of our molecular mechanical study was to establish the thermodynamic stabilities of the compounds involved in the eight-membered ring to five-membered ring rearrangement[5] as well as the compounds involved in the thiono-thiolo rearrangement of the thiophosphoric ester[6].

5.2 Experimental

The group of structurally related phosphoramidates, discussed in the preceding chapters, was further studied by molecular mechanical calculations.

Hyperchem software was used to perform the molecular mechanical calculations. The default force field in Hyperchem is MM+ (Mmplus). MM+ is an extension of MM2 which was developed by Allinger and co-workers.[7,8,9] Hyperchem's MM+ force field employs the latest MM2 (1991) parameters and atom types with the 1977 functional form[7,8,9].

The MM+ force field internally makes use of ergs for energy and reports its force constants in units of millidynes per Ångstrom. For example, a factor of 71.94 must be multiplied to MM+ stretching force constants for comparison with stretching force constants for the other force fields. Hyperchem reports all energy results in energy units of kcal/mol.

The interaction potential describes both bonding and non-bonding interactions. The interaction potential calculated by MM+ includes energy terms for bond stretching, bond dipoles, angle bending, dihedrals, Van der Waals interactions as well as a bond stretching and angle bending cross term.

A description of how the energetic terms are calculated is included as described in the Hyperchem Manual.

Bond Stretching

MM2 uses a cubic stretch term:

$$E_{bond} = 143.88 \Sigma 0.5 K_r(r-r_0)^2[1+ CS(r-r_0)]$$ **Equation 5. 2**

The cubic stretch term is a factor CS times the quadratic stretch term. This constant CS can be set to an arbitrary value. The default value for MM2 and MM+ is CS = -2.0.

Two r_0 values are given for each MM+ bond, r_0^A and $r_0^{B.}$ If r_0^B is available (has a non-zero value in the parameter file) then it is used in preference to the normal r_0^A for bonds where atom i and j have at least two hydrogen atoms directly attached to them.

Bond Dipoles

MM+ calculations do not have an electrostatic charge-charge interaction nor define a set of atomic charges for atoms. The electrostatic contributions come from defining a set of bond dipole moments associated with polar bonds. The MM+ dipole is calculated by **Equation 5.3**.

$$E_{dipole} = 14.39418 \varepsilon \Sigma \mu_i\mu_j [(\cos \chi - 3\cos\alpha_i\cos\alpha_j)/R_{ij}^3]$$ **Equation 5. 3**

The center of the dipole is defined to be the midpoint of the bond and two dipoles μ_i and μ_j, separated by R_{ij} (**Figure 5.1**).

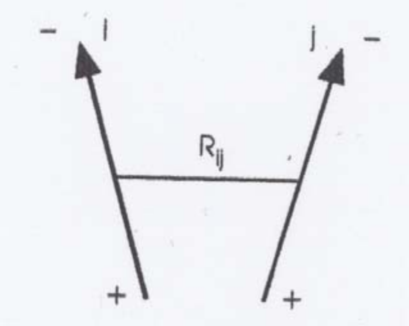


Figure 5.1

Where ε is the dielectric constant. Hyperchem uses the MM2 value of 1.5. The angle χ is the angle between the two dipole vectors and α_i and α_j are the angles that the two dipole vectors make with the R_{ij} vector. The constant 14.39418 converts ergs to kcal/mol.

Angle Bending

Equation 5.4 is used for the angle bending energy.

$$E_{\text{bond angle}} = 0.043828 \, \Sigma \, 0.5 \, K_\theta \, (\theta - \theta_0)^2 \, [\, 1 + SF \, (\theta - \theta_0)^4] \qquad \textbf{Equation 5. 4}$$

MM+ includes a sextic angle bending term. This term is a scale factor SF times the quadratic bending term. The constant 0.043828 converts the MM+ bending constants expressed in millidynes-A per radian^2 to kcal/mol per degree^2.

Bond Stretch and Angle Bending Cross Term

MM+ includes coupling between bond stretching and angle bending. If the angle is defined to include atoms i, j and k, where k is the central atom, then MM+ couples stretching of the ik and jk bonds with the angle:

$$E_{\text{stretch-bend}} = 2.51118 \sum K_{sb} \, (\theta - \theta_0)_{ijk} \left[(r - r_0)_{ik} + (r - r_0)_{ij}\right] \qquad \textbf{Equation 5. 5}$$

If atoms *i* or *j* is a hydrogen, the deformation is considered to be zero. Thus, no stretch-bend interaction is defined for XH_2. The stretch-bend force constants are incorporated into the programme and cannot be changed. If R is not a hydrogen, the following values are used for the stretch-bend force constants:

$K_{sb} = 0.120$ for XR_2 where X is in first long row

$K_{sb} = 0.090$ for XRH

$K_{sb} = 0.250$ for XR_2 where X is in second long row

K_{sb} = -0.400 for XRH

The constant 2.51118 converts between MM+ stretch-bend force constants expressed in millidynes per radian and Hyperchem's default, kcal per degree.

Out-of-Plane Bending

An sp^2 hybridized atom tends to be co-planar with its attached atoms. This effect is accounted for by improper torsions in other force fields and by out-of-plane-bending interactions in MM+.

Consider the situation illustrated in figure 5.2, involving an atom X that is sp^2 hybridized. Y is the projection of X onto the ABC plane.

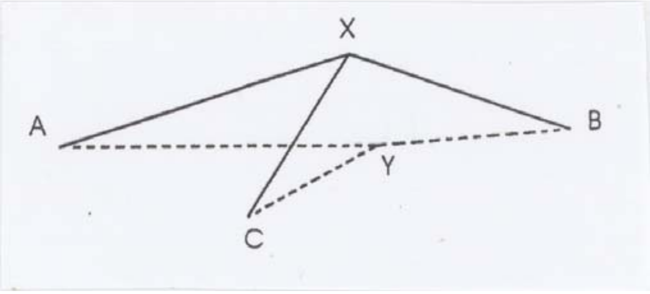


Figure 5. 2

When the central atom (X) is sp^2 hybridized, the angle bending calculations are modified to use the in-plane angles AYB, AYC and BYC in equation 5.4 with the standard force constants rather than the standard angles AXB, AXC and BXC. Out-of-plane components are computed as well, for the out-of-plane angles XAY, XBY and XCY. These last three calculations also use equation 5.4, but with θ_0 equal to 0 and special out-of-plane bending constants, K_θ.

Dihedrals

The dihedral angle or torsional energy interaction in MM+ is of the general form of equation 5.6 but explicitly includes n=1,2 and 3 with a phase angle of $\Phi_0 = 0$:

$$E_{dihedral} = \sum V_n/2\ [1 + \cos(n\Phi - \Phi_0)]$$ **Equation 5. 6**

The MM+ force field uses special values for the torsional force constants when the atoms are in a four-membered ring.

Van der Waals

The MM+ van der Waals interactions do not use a Lennard-Jones potential but combine an exponential repulsion with an attractive $1/R^6$ dispersion interaction. The basic parameters are a van der Waals radius r_i^* for each atom type and a hardness parameter ε_i that determines the depth of the attractive well and how easy (or difficult) it is to push atoms close together. There are interactions for each nonbonded ij pair, including all 1-4 pairs. The parameters for a pair are obtained from individual atom parameters as follows:

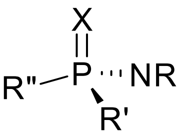
$$r_{ij}^* = r_i^* + r_j^*$$

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{0.5}$$

The van der Waals interaction is then calculated using **Equation 5.7**.

$$E_{\text{van der Waals}} = \sum_{ijvdW} \varepsilon_{ij}(2.9 \times 10^5 \exp(-12.5\rho_{ij}) - 2.25\, \rho_{ij}^{-6}) \qquad \textbf{Equation 5. 7}$$

Hyperchem's MM+ does not include parameters for the phosphorous-nitrogen bond in the chemical environment of interest (**Figure 5.3**).



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X = O, S
R = alkyl
R' = *N*-aryl, *N*-alkyl ,alkoxy
R" = *N*-aryl, *N*-alkyl

Figure 5.3 General structure of compounds discussed in this chapter.

The new atom types, which were introduced, are listed in **Table 5.6**. Column 3 in **Table 5.6** contains the lines that were added to describe the connectivities of the new atom types. All tables containing the new force field parameters are appended at the end of the chapter.

The geometries of all the compounds were optimized with MM+ using a conjugate gradient algorithm, Polak-Ribiere.

The structural data from the crystal structures were used to set up the new force field. Crystal structures were not available for all the compounds in the series and in such cases the structural data of a structurally closely related compound e.g. PELRED, SACWOI, SACYEA from the Cambridge Database[10] were used.

The energies of a series of phosphoramidates were calculated. All the structures listed in **Table 5.1** were optimized in order to prepare a force field that can be applied to the phosphortriamidates in general.

5.3 Results and Discussion

The MM+ parameter files only included parameters for interactions with lone pairs on sp^3 oxygen (e.g. in alcohol), sp^3 nitrogen (e.g. in tertiary amine), furan oxygen, oxime nitrogen and pyridine nitrogen. No lone pairs were added to sp^2 oxygen, sp^2 nitrogen and sulphur or halogens. This is a matter of great uncertainty and confusion. Numerous authorities[11] on the subject of molecular modeling were consulted regarding the treatment of the lone pairs in Hyperchem. All agreed that in principle, the lone pairs should be added, but it seems that Hyperchem treats this differently. Hypercube[a] was contacted in this regard with no success.

Structure optimization resulted in exactly the same geometry, regardless of the in- or exclusion of lone pairs to the appropriate atoms, but the calculated energies were completely different. A difference between these two scenarios

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[a] Company who developed HyperChem software

was expected since many more interactions are involved when lone pairs are added. The size of the electrostatic energy term increases significantly when the lone pairs are included. This is due to the interaction of all the pairs of dipoles in the compound. Another approach is to treat the lone pairs as if they were hydrogen atoms. Replacement of the lone pairs by hydrogen atoms resulted in the distortion of the bond distances and bond angles, where oxygen, sulphur and nitrogen are involved. The bending energy term overshadowed all the other energy terms.

All the structures of the compounds discussed in this chapter were optimized by the same force field; therefore the decision was made to leave out the lone pairs. Reliable results were obtained in the reproduction of the crystal structures, without the addition of lone pairs.

The new force field produced a reliable representation of the real geometries of the phosphoramidates in the different chemical environments under investigation. We were only interested in the relative thermodynamic stabilities of the compounds, especially the eight-membered ring and five-membered ring isomers.

Table 5.1 is included for a quick reference to the different structures that are discussed in this chapter. The same numbering system was used in the preceding chapters.

For the P (O)*N*-Phenyl series (column A) the ^{1}H, ^{31}P and ^{15}N –NMR as well as the crystal data revealed a decrease in the N-P-N bond angles and an increase in the P-N bond distances. The nitrogen atoms became less planar (more pyramidal) with the introduction of another ring. The planarity of the nitrogen is indicated by the sum of the three angles around nitrogen. A sum close to 360 degrees implicates a planar nitrogen as in the triamidate precursor **1**. The smaller sum of 326 degrees for the tricyclic compound **4**, indicated a more pyramidal nitrogen. The bond angles and bond distances of the triamidate series are listed in **table 5.2**

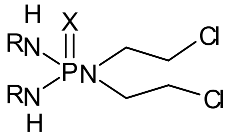
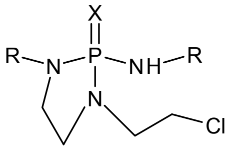
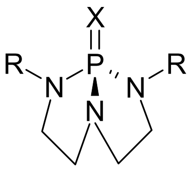
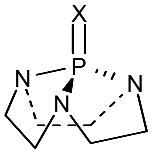
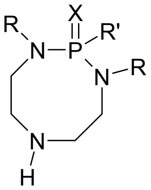
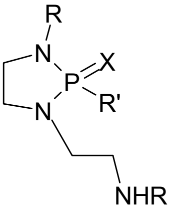
“username” of compound	Number of Compound	Structure
Substrate	0 X=O 8 X=S	$Cl_2P(X)(NCH_2CH_2Cl)_2$
Triamidate	1a X=O, R=Ph 1f X=O, R=Bz *9a X=S, R=Ph 9b X=S, R=Bz	
Monocyclic	2a X=O, R=Ph 2f X=O, R=Bz *10 X=S, R=Ph *10 X=S, R=Bz	
Bicyclic	3a X=O, R=Ph 3f X=O, R=Bz 11a X=S, R=Ph *11b X=S, R=Bz *19 X= lone pair, R=Ph	
Tricyclic	4 X=O 21 X=S	
8ring	5a X=O, R=Ph , R’=OEt 5f X=O, R=Bz , R’=OMe *15 X=S, R=Ph , R’=OMe (thiono) *17 X=O, R’=SMe, R=Ph (thiolo)	
5ring	6a X=O, R=Ph, R’=OEt 6f X=O, R=Bz, R’=OMe 16 X=S, R=Ph, R’=OMe (thiono) 17a X=O, R’=SMe, R=Ph (thiolo)	

Table 5.1 List of the labelled structures of all compounds which were discussed in this chapter. *Compounds that were not isolated.

Compound	Triamidate	Monocyclic	Bicyclic	Tricyclic
Av P-N bond distance (Exp) /Å	1.639	1.646	1.663	1.673
Av P-N bond distance (Calc) /Å	1.651	1.6532	1.655	1.658
Av N-P-N angle (Exp) /°	105.7	105.53	102.1	100.9
Av N-P-N angle (Calc) /°	102.097	101.400	100.380	98.132
Sum of angles around endocyclic N exp	359.39	350.1	336.04	
Sum of angles around endocyclic N calc	359.51	357.27	347.13	332.59

Table 5. 2 Selected bond distances and bond angles for the P(O)N-Phenyl series.

This trend was also observed in the geometries of the calculated structures listed in **table 5.2**, however the changes in P-N bond distance and the bond angle were much more subtle. It was expected that the nonrigid triamidate **1a** and the highly strained bicyclic compound **3a** cannot be modeled exactly with the same set of parameters, because of the big differences in the geometry of the nitrogen atom. The changes in hybridization is also clear from the calculated geometries.

The geometries of the two compounds that were of interest, the eight-membered ring **5a** and five-membered ring **6a** compounds correspond very well with the experimental data. Selected bond distances, bond angles and torsion angles are listed in **Table 5.3.** All the calculated torsion angles involving the phosphorus tetrahedron or a nitrogen atom correspond with the experimental values. Some of the calculated torsion angles are of the same order of magnitude as the experimental values but of opposite sign. This can be explained as follows: when the two structures are superimposed, the orientation of the N-C bond are in opposite directions i.e. when it is "up" in the crystal structure, it is "down" in the calculated structure and vice verca. The sign of the torsion angles does not influence the energy calculation. No parameters were added for torsion angles. For the torsion angles where the new atom types were involved, the default values in Hyperchem were used.

The calculated values for the bond angles and bond distances are in good agreement with the experimental values. This result demonstrated that the amended force field is a reliable model to predict the geometries of the other derivatives of the eight-membered ring and the five-membered ring isomers.

8-RING <u>5a</u>	**EXP**	**CALC**	**5-RING <u>6a</u>**	**EXP**	**CALC**
Bond distances /Å					
P=O	1.466	1.446	P=O	1.476	1.442
P-N$_1$	1.653	1.665	P-N$_1$	1.662	1.661
P-N$_3$	1.678	1.666	P-N$_2$	1.648	1.648
P-Oet	1.574	1.594	P-OEt	1.571	1.578
N$_1$-C	1.484	1.488	N$_1$-C	1.474	1.485
N$_3$-C	1.479	1.486	N$_3$-C	1.462/1.464	1.463/1.469
N$_1$-C$_a$	1.435	1.422	N$_1$-C$_a$	1.399	1.425
N$_3$-C$_a$	1.432	1.421	N$_3$-C$_a$	1.376	1.352
Bond angles /°					
P-O-C	119.2	125.7	P-O-C	121.5	124.9
O=P-O	114.2	110.2	O=P-O	107.2	113.2
O=P-N$_1$	111.3	112.1	O=P-N1	116.7	112.3
O=P-N$_3$	115.6	113.8	O=P-N$_2$	118.4	117.1
O-P-N$_1$	106.3	104.1	O-P-N$_1$	110.2	108.1
O-P-N$_3$	101.5	102.5	O-P-N$_2$	109.2	109.2
C-N$_1$-C$_a$	118.5	118.5	C-N$_1$-C$_a$	121.2	121.6
C-N$_3$-C$_a$	117.9	120.3	C-N$_2$-C	119.0	122.5
P-N$_1$-C	116.1	116.2	P-N$_1$-C	112.7	109.5
P-N$_1$-C$_a$	124.7	122.7	P-N$_1$-C$_a$	125.1	126.1
P-N$_3$-C	118.9	115.7	P-N$_2$-C$_{exo}$	119.8	124.9
P-N$_3$-C$_a$	121.1	123.6	P-N$_2$-C$_{endo}$	111.3	112.6
C-N$_2$-C	117.5	114.5	C-N$_3$-C	125.1	119.9
N$_1$-P-N$_3$	107.1	113.2	N-P-N	94.8	95.4
Torsion angles /°					
O=P-O-C	43.5	49.4	O=P-O-C	179.5	177.1
O=P-N$_1$-C	30.3	-42.1	O=P-N$_1$-C	-125.1	-101.3
O=P-N$_1$-C$_a$	-159.2	119.3	O=P-N$_1$-C$_a$	66.7	59.7
O=P-N$_3$-C	-108.3	40.8	O=P-N$_2$-C$_{endo}$	104.0	119.0
O=P-N$_3$-C$_a$	54.9	-146.3	O=P-N$_2$-C$_{exo}$	-41.4	-59.492
P-N$_1$-C-C	84.2	-51.4	P-N$_1$-C-C	18.2	34.632
P-N$_3$-C-C	83.3	94.9	P-N$_2$-C$_{endo}$-C	32.5	-20.745
C$_a$-N$_1$-C-C	-86.9	146.4	C$_a$-N$_1$-C-C	-173.0	163.379
C$_a$-N$_3$-C-C	-80.4	-78.4	C$_{exo}$-N$_2$-C-C	178.2	157.82
N$_1$-P-N$_3$-C	16.4	-88.8	N$_1$-P-N$_3$-C	0.6	-19.8
N$_3$-P-N$_1$-C	-96.9	88.4	N$_3$-P-N$_1$-C	20.9	0.1
C$_a$ = aromatic carbon, C$_{endo}$= carbon inside five-membered ring, C$_{exo}$= carbon outside five-membered ring.					

Table 5.3 Selected bond angles, bond distances and torsion angles of eight (**<u>5a</u>**)- and five-membered (**<u>6a</u>**) ring compounds.

The calculated energies of the 8-membered ring to 5-membered ring isomers for all the different derivatives are listed in **Table 5.4.** The relative energies confirmed that the rearrangement is thermodynamically controlled. The five-membered ring isomer has in each case a lower total strain energy than the eight-membered ring isomer.

"username"	Compound no.(Table 5.1)	**Eight-membered ring** kcal/mol	Compound no. (Table5.1)	**Five-membered ring** kcal/mol
P(O)N-Phenyl	**5a**	13.257	**6a**	7.163
P(O)N-Benzyl	**5f**	7.147	**6f**	5.731
P(S)N-Phenyl	**15**	13.974	**16**	6.661
P(S)N-Benzyl *	**15x**	10.866	**16x**	2.832

Table 5. 4 Calculated energies in kcal/mol for eight-membered ring and five-membered ring isomers.

The thiono-thiolo isomers had comparable potential energies. Rows A and B from **Table 5.5** indicate that for the *N*-Phenyl derivatives the thiolo isomer had a slightly lower potential energy than the thiono isomer for both the eight- end five-membered ring isomers. The last two rows in the table indicated more stable *N*-Benzyl substituted thiono isomers for both the five-membered and eight-membered ring isomers.

For the thiono as well as the thiolo isomers the calculated energies suggest that the five-membered ring isomer is thermodynamically more stable than the eight-membered ring compound. From **Table 5.5** it is clear that there is a consistency in the trend of the calculated results for the whole series of rearrangement products.

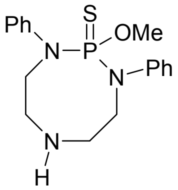
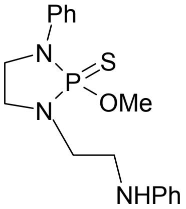
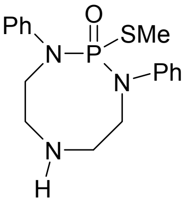
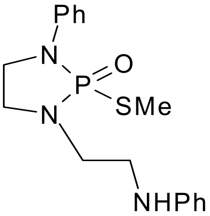
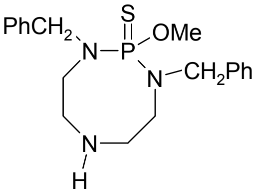
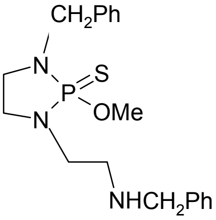
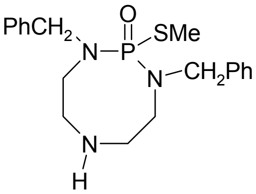
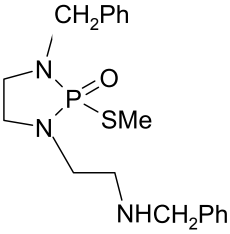
	“username”	E No.	F 8-ring Energies in kcal/mol	G no.	H 5-ring Energies in kcal/mol
A	**P(S)N-Phenyl thiono**	**15a** 	**13.974**	**16a** 	**6.661**
B	**P(O)N-Phenyl thiolo**	**22** 	**12.407**	**23** 	**5.688**
C	**P(S)N-Benzyl thiono**	**15f** 	**10.866**	**16f** 	**2.832**
D	**P(O)N-Benzyl thiolo**	**24** 	**12.644**	**25** 	**6.060**

Table 5.5 Calculated energies in kcal/mol for all thiono and thiolo phosphoric esters.

The following tables contain lists of all the parameters that were added to prepare the new force field.

Element	Description in chem.rul file
P	; phosphorus (P=O) connected to (=O)(-N)(-N)(-N)
P	; phosphorus (P=S) connected to (=S)(-N)(-N)(-N)?
P	; phosphorus P(O)NCl2 connected to (=O)(-N)(Cl)(-Cl)?
N	; phosphoramide connected to (-C)(-C)(-P)?
N	; phosphoramide connected to (-C)(-C)(-P)?
O	; phosphoryl connected to (=P)?
O	; phosphate ester connected to (-C)(-P)?
S	; thiophosphoryl connected to (=P)?
S	; phosphate thio ester connected to (-C)(-P)?

Table 5. 6 New atom types added to *chem.rul*

TYPE	MASS	REMARK
n5	14.003	73. N PHOSPHORAMIDE
n8	14.003	74. N PHOSPHORAMIDE
Po	30.994	77. P P=O phosphoryl
Ps	30.994	78. P P=S thiophosphoryl
Px	30.994	79. P P(O)NCl2
Op	15.994	80. O O=P
Sp	31.972	81. S S=P
Om	15.994	82. O P-OMe
Sm	31.972	83. S P-SMe

Table 5. 7 Changes made to *mmptype.txt* to list new atom types.

T1	T2	KS	L0	L1	DIPOLE
H	op	4.600	0.942	0.000	-1.115
H	sp	3.800	0.600	0.000	0.389
Px	op	6.500	1.456	0.000	-0.650
Px	sp	3.000	1.889	0.000	-0.650
Px	n5	6.400	1.618	0.000	0.950
Px	cl	3.200	2.012	0.000	1.950
Po	cl	3.200	2.012	0.000	1.950

Po	op	3.000	1.437	0.000	0.970
Ps	sp	3.100	1.930	0.000	0.900
Po	n5	6.200	1.637	0.000	0.950
Ps	n5	6.200	1.670	0.000	0.950
Po	n8	6.200	1.665	0.000	0.950
Ps	n8	6.200	1.670	0.000	0.950
n8	ca	6.320	1.410	0.000	1.300
n5	c4	5.100	1.460	0.000	0.040
n8	c4	5.100	1.470	0.000	1.470
Po	sm	2.900	1.800	0.000	0.970
Po	om	2.900	1.571	0.000	0.970
Ps	om	2.900	1.571	0.000	0.900
Om	c4	5.350	1.571	0.000	0.440
Sm	c4	3.200	1.815	0.000	0.000
Po	sm	3.100	2.024	0.000	0.830
n8	co	6.400	1.352	0.000	-0.290

Table 5. 8 Changes made to mmpstr.txt for bond stretching.

T1	**T2**	**T3**	**KS**	**TYPE1**	**TYPE2**	**TYPE3**
Op	po	n5	0.315	119.103	0.000	0.000
Op	px	n5	0.330	116.680	0.000	0.000
Op	po	n8	0.350	113.565	0.000	0.000
Sp	ps	n5	0.330	121.100	0.000	0.000
Sp	px	n5	0.300	121.300	0.000	0.000
Sp	ps	n8	0.300	113.850	0.000	0.000
Op	px	cl	0.560	112.650	0.000	0.000
Sp	px	cl	0.445	113.550	0.000	0.000
Sp	ps	cl	0.500	110.000	0.000	0.000
n8	ps	cl	0.500	108.000	0.000	0.000
n5	ps	cl	0.500	108.000	0.000	0.000
Op	po	cl	0.500	110.000	0.000	0.000
Cl	px	cl	0.710	99.910	99.960	0.000
Cl	po	cl	0.710	99.910	99.960	0.000
Cl	px	n5	0.450	108.00	105.00	0.000
Cl	po	n5	0.450	108.00	105.00	0.000
n8	po	n5	0.680	96.320	95.710	0.000
n8	po	n8	0.455	114.420	0.000	0.000
n8	ps	n5	0.690	95.410	0.000	0.000
n8	ps	n8	0.500	114.910	0.000	0.000
n5	po	n5	0.520	111.420	102.200	103.120
n5	ps	n5	0.520	111.420	102.200	103.120
Op	po	om	0.455	114.200	107.200	0.000
c4	n5	c4	0.380	119.000	111.340	0.000
Px	n5	c4	0.375	120.890	0.000	0.000
Po	n5	c4	0.375	120.890	110.300	0.000
Ps	n5	c4	0.320	123.600	109.350	0.000
Ps	n5	hv	0.440	110.000	0.000	0.000
Po	n8	ca	0.310	125.500	0.000	0.000
Ps	n8	ca	0.300	127.610	0.000	0.000
Ps	n8	c4	0.360	109.610	0.000	0.000
Po	n8	c4	0.530	110.020	0.000	0.000
Po	n8	hv	0.430	115.600	0.000	0.000
Ps	n8	hv	0.430	115.600	0.000	0.000

Po	n5	hv	0.440	110.000	0.000	0.000
c4	n5	hv	0.430	115.600	0.000	0.000
c4	n5	hn	0.695	106.690	0.000	0.000
Ca	n8	hv	0.420	116.000	0.000	0.000
c4	n8	ca	0.690	121.200	0.000	0.000
n5	c4	c4	0.450	112.890	0.000	0.000
n5	c4	ca	0.500	108.500	0.000	0.000
n5	c4	h	0.360	109.500	0.000	0.000
n8	c4	h	0.530	110.400	0.000	0.000
n8	ca	ca	0.695	120.000	0.000	0.000
Om	po	n5	0.530	111.300	115.6	0.000
Om	c4	h	0.695	109.470	0.000	0.000
Om	c4	c4	0.695	109.470	0.000	0.000
n8	c4	c4	0.500	105.600	0.000	0.000
n5	po	om	0.360	109.000	0.000	0.000
n8	po	om	0.500	106.300	101.500	110.200
Om	ps	n5	0.360	109.000	119.200	0.000
Sm	po	op	0.400	121.500	119.200	0.000
Ps	om	c4	0.400	121.500	119.200	0.000
Po	sm	c4	0.400	121.500	119.200	0.000
Po	om	c4	0.400	121.500	119.200	0.000

Table 5. 9 Changes made to *mmpben.txt* for angle bending.

C	**A**	**COPB**
Ca	n8	0.050
n8	Ca	0.050
n8	Hv	0.050
n8	Po	0.050
n8	Ps	0.050
n5	Hv	0.050
n5	c4	0.050
Po	Op	0.050
Ps	Sp	0.050
Op	Po	0.050
Sp	Ps	0.050
Px	Op	0.050
Op	Px	0.050
Px	Sp	0.050
Px	Sp	0.050
n5	Px	0.050
n5	Po	0.050
n5	Hn	0.050
n5	Ps	0.050
n8	c4	0.050
Sm	c4	0.050
Om	c4	0.050
Ps	Om	0.050
Ps	Sm	0.050
Po	Sm	0.050
Po	Om	0.050

Table 5.10 Changes made to *mmpoop.txt* for out-of-plane bending.

TYPE	RSTAR	EPS
Po	2.2000	0.1680
Ps	2.2000	0.1680
Px	2.2000	0.1680
Op	1.7400	0.0660
Sp	2.1100	0.2020
Om	1.7400	0.0500
Sm	2.1100	0.2020
n5	1.8200	0.0550
n8	1.8200	0.0550

Table 5.11 Changes made to *mmpnbd.txt* for van der Waals radii.

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