Molecular Mechanics: Pentaco-ordinate Phosphorus in MM2. Parameters for the 1–3 Interactions. Evaluation Tests

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A new set of parameters for 1–3 interactions around the pentaco-ordinate phosphorus atom adapted to Allinger's 1977 force field, has been worked out and tested on phosphorane structures.

In molecular mechanics, when dealing with compounds of high co-ordinate atoms (*i.e.*, >4), several problems arise which common programs do not take care of. To account for the stability difference of various possible geometries, 1–3 interactions around the central atom need to be reintroduced, at least for co-ordination number 5. Deiters *et al.*[1] in their extension of Allinger's program MM1[2] to pentaco-ordinate phosphorus compounds, have simulated the repulsion between two bonding electron pairs by a van der Waals type interaction between the atoms in positions 1 and 3, situated at reduced distances from the central atom. The reduction factors R_{P-X} are essentially based on the central atom–ligand atom electronegativity difference.

We have modified the program MM2[3] in keeping with the philosophy of Deiters *et al.*; the reduction factors previously determined for MM1 were no longer of use so we gave them new values. The new set of parameters was then tested for validation and we now report the evaluation and tests.

Calculations of the reduction factors R_{P-X} for the Allinger's 1977 force field (MM2) have been performed in such a way as to obtain the same values as those found with Allinger's 1973 force field (MM1) for the ratios of 1–3 interaction energies for pairs of different X atoms (X = H,O,N,C). The atoms were first distributed on the vertices of the ideal trigonal bipyramid and then around the ideal square pyramid as described by Deiters *et al.* for phosphorus.[1] The values obtained were the same and the set is reported in Table 1.

Using the MM2 program, geometries around the phosphorus atom in molecules (**A**) and (**B**) (Figure 1) have been optimised with the help of the reduction factors given in Table 1 and the results compared with both the experimental data[4,5] and the calculations of Deiters *et al.*[1] (Table 2). The scale factor *D*, which puts the 1–3 interaction energy terms on the same scale as the other terms, has been found also to give the smallest deviation, δ, for the value 0.085. The agreement with other results is good. The largest deviation concerns the

Table 1. Reduction factors for 1–3 interactions around phosphorus in MM1 (ref. 1) and MM2 programs.

X	R_{P-X} (MM1)	R_{P-X} (MM2)
H	0.550	0.51
N	0.681	0.78
O	0.822	0.76
C	0.550	0.47

Table 2. Bond lengths (Å) and angles (°) around the phosphorus atom in compounds (**A**) and (**B**). δ has been evaluated as in ref. 1.

	(**A**)			(**B**)		
	Exp.[4]	Deiters[1]	This work	Exp.[5]	Deiters[1]	This work
P–O	1.709	1.71	1.71	1.700	1.69	1.71
P–N	1.671	1.68	1.66	1.690	1.68	1.69
P–H	1.47	1.46	1.45		1.46	1.45
O–C	1.441	1.44	1.41	1.434	1.44	1.41
N–C	1.448	1.45	1.45	1.500	1.47	1.46
C–C	1.518	1.51	1.52	1.545	1.54	1.53
O–P–O′	177.0	179.3	179.1	176.6	176.9	178.7
N–P–N′	131.7	125.2	120.9	123.3	129.6	128.4
O–P–N	88.2	90.3	89.8	89.2	90.8	89.5
O–P–N′	90.5	89.4	90.6	92.4	90.5	91.1
N–P–H	114.1	117.4	119.6		115.2	115.8
O–P–H	91.5	90.3	89.5		88.5	89.3
P–O–C	111.6	112.0	111.6	111.9	112.5	111.7
P–N–C	119.6	116.7	115.9	115.4	117.8	115.2
O–C–C	107.2	107.1	105.0	103.2	108.8	105.0
N–C–C	102.0	104.4	103.7	100.3	101.7	102.9
C–N–H	118.9	119.7	119.8			
P–N–H	121.0	123.6	121.4			
δ		0.05 ($D = 0.10$)	0.06 ($D = 0.085$)		0.05 ($D = 0.075$)	0.04 ($D = 0.085$)

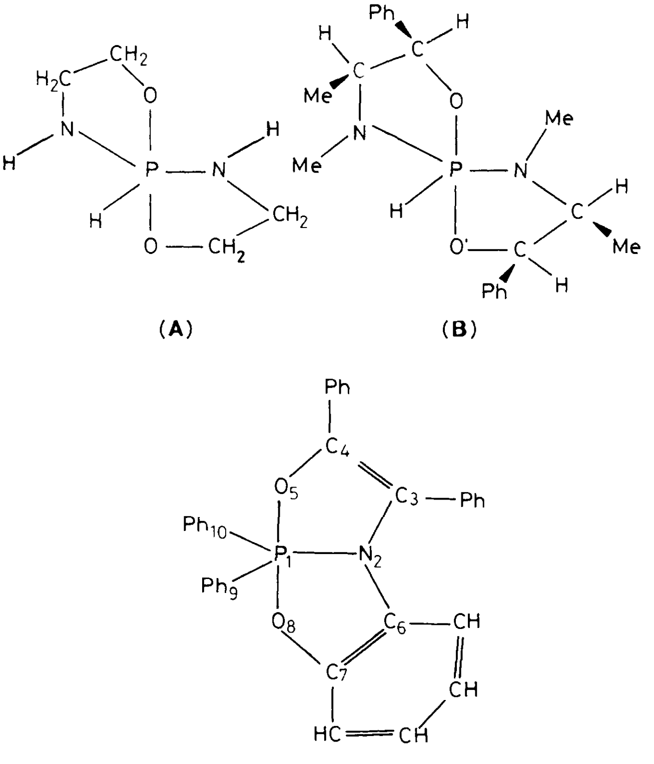

Figure 1. Test molecules for reduction factors used in 1–3 interactions around phosphorus in Allinger's 1977 force field. Molecules (**A**) and (**B**), see ref. 1; molecule (**C**), see ref. 7.

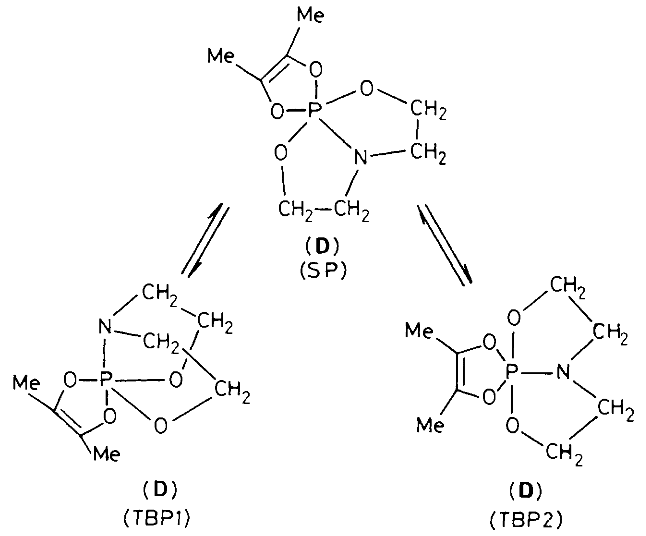

Figure 2. Scheme of the pseudorotation process for molecule (**D**) (see ref. 8).

N_{eq}–P–N_{eq} angle which, in both calculations, is either too small (**A**) or too large (**B**) when compared to *X*-ray structure values. An explanation for this could be that this angle is especially sensitive to packing forces. A recent paper of Lattman *et al.*[6] provides an argument to that effect; they reported that the N_{eq}–P–N_{eq} angle in the cyclenphosphorane (a tetracyclic phosphorane) moves from 138° (solid state) to 155° (gas phase).

Our calculations have been extended to the bicyclic phosphorane (**C**) (Figure 1), which is one of the four compounds of this type for which the *X*-ray structure has been determined.[7] Agreement with reported bond lengths and angles is good although, perhaps due to a packing effect, the pivot atom of a phenyl group (C-10) is displaced in the solid state. Unfortunately, our calculations have shown that there are inconsistencies between some reported bond lengths and the atom co-ordinates concerned (N for example). We assume that the bond lengths and angles are accurate and some co-ordinates are erroneous.

Geometries being reasonably well reproduced, the parameters have also been tested to check if they were giving

Table 3. Bond lengths (Å) and angles (°) around the phosphorus atom in compound (**C**). For experimental data see ref. 7. δ has been evaluated as in ref. 1.

	Exp.[7]	This work
P–O(5)	1.700	1.724
P–O(8)	1.763	1.764
P–N(2)	1.703	1.679
P–C(9)	1.811	1.802
P–C(10)	1.818	1.803
O(5)–P–O(8)	171.6	179.8
O(5)–P–C(9)	94.7	89.9
O(5)–P–C(10)	89.7	90.1
O(8)–P–C(9)	93.3	90.1
O(8)–P–C(10)	89.7	89.7
C(9)–P–C(10)	112.8	123.5
N(2)–P–O(5)	86.6	88.8
N(2)–P–O(8)	87.6	91.3
N(2)–P–C(9)	116.5	117.0
N(2)–P–C(10)	130.6	119.4
		$\delta = 0.07$ (for $D = 0.085$)

correct relative steric energies. An n.m.r. study of molecule (**D**) (Figure 2) by Denney *et al.*[8] has shown that, at low temperature, the most stable conformation is trigonal bipyramidal, the nitrogen atom being axial (BPT1). At ambient temperature, equivalence of the protons of the methyl groups suggests the existence of a pseudorotation process (1) leading from TBP1 to TBP1* (same geometry but with exchange of the Me positions) through a higher energy trigonal bipyramid BPT2 and two identical square pyramids (SP and SP*). The estimated barrier in solution, is reported to be 46.0 kJ mol^{-1}.

$$\mathrm{TBP1} \rightleftarrows \mathrm{SP} \rightleftarrows \mathrm{TBP2} \rightleftarrows \mathrm{SP^*} \rightleftarrows \mathrm{TBP1^*} \tag{1}$$

Our results agree well with the n.m.r. conclusions as the steric energies found for the optimized geometries of TBP1, SP and TBP2 are, respectively, 99.1, 106.7, and 109.8 kJ mol^{-1}.

Estimation of conformational barriers is not an easy task and depends on the way the reaction co-ordinate (Berry co-ordinate here) is described. Within the very simple scheme of simultaneous closing of the N_{ax}–P–O_{ax} angle and opening of the O_{eq}–P–O_{eq} angle the barrier on the way from TBP1 to SP has been evaluated as 18 kJ mol^{-1} (nitrogen remaining pyramidal). The highest barrier occurs between SP and BPT2 and is more difficult to estimate because of the change in hybridisation of the nitrogen atom.

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