

A Molecular Mechanics Approach to Mapping the Conformational Space of Diaryl and Triarylphosphines

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SUPPLEMENTARY INFORMATION

A. NMR SPECTRAL DATA

Chemical shifts are in ppm relative to SiMe₄ (¹H and ¹³C) or 85 % H₃PO₄ (³¹P). For ¹³C spectra, numbers in parentheses are P-C coupling constants in Hz.

1. 2-ⁱPrC₆H₄Br. ¹H NMR (CDCl₃): 7.0-7.5 (4H, m, Ph), 3.35 (1H, sept, CHMe₂), 1.23 (6H, d, CHMe₂, J = 6.8 Hz); ¹³C NMR (CDCl₃): 124.3, 126.6, 127.2, 127.6, 132.7, 147.3, 32.8, 22.7.

2. 2-^tBuC₆H₄I. ¹H NMR (CDCl₃): 6.83-8.02 (4H, m, Ph), 1.55 (s, ^tBu); ¹³C NMR (CDCl₃): 95.1, 127.5, 127.6, 127.9, 143.5, 150.1, 36.7, 29.8.

3. (2-EtC₆H₄)₃P. ¹H NMR (CDCl₃): 7.20-7.31 (6H, m, H₃, 4), 7.05 (3H, m, H₅), 6.73 (3H, dd, H₆), 2.59 (6H, q, CH₂CH₃, J = 7.5 Hz), 1.12 (9H, t, CH₂CH₃); ³¹P NMR (CDCl₃): -33.7; ¹³C NMR (CDCl₃): 134.9 (12, C1), 148.5 (26, C2), 128.1 (5, C3), 128.8 (C4), 126.0 (5, C5), 133.9 (C6), 27.4 (23, CH₂CH₃), 15.1 (3, CH₂CH₃).

4. (2-ⁱPrC₆H₄)₃P. ¹H NMR (CDCl₃): 7.20-7.35 (6H, m, H₃, 4), 7.00 (3H, m, H₅), 6.74 (3H, dd, H₆), 3.62 (3H, m, CHMe₂, J = 7.5 Hz), 1.08 (18H, d, CHMe₂); ³¹P NMR (CDCl₃): -33.3; ¹³C NMR (CDCl₃): 134.8 (13, C1), 153.1 (24, C2), 125.3 (5, C3), 129.0 (C4), 125.9 (C5), 134.0 (C6), 32.8 (25, CHMe₂), 23.7 (CHMe₂).

5. (2-MeC₆H₄)₂(2-^tBuC₆H₄)P. ¹H NMR (CDCl₃): 6.80 (2H, dd, H₆), 6.98-7.31 (9H, m, H₃-5, 3'-5'), 7.48 (1H, m, H_{6'}), 2.30 (6H, s, Me), 1.51 (9H, s, ^tBu); ³¹P NMR (CDCl₃): -22.1; ¹³C NMR (CDCl₃): 125.8, 126.1, 126.2 (7), 128.3, 129.0 (1), 130.0 (4), 133.2 (br), 133.5 (23), 133.8 (br), 136.8 (14), 137.1 (2), 141.9 (26), 155.0 (26), 21.5 (20, Me), 37.3 (CMe₃), 31.9 (12, CMe₃).

6. (2-MeC₆H₄)₂MeP. ¹H NMR (CDCl₃): 7.11-7.20 (8H, m, H₃-6), 2.39 (6H, s, Me), 1.90 (3H, d PMe, J(PH) = 4.0 Hz); ³¹P NMR (CDCl₃): -46.5; ¹³C NMR (CDCl₃): 137.8 (12, C1), 141.8 (25, C2), 129.9 (5, C3), 128.4 (C4), 126.1 (C5), 130.7 (C6), 11.1 (13, PMe), 21.0 (21, Me).

- 7. (2-MeC₆H₄)₂^tBuP.** ¹H NMR (CDCl₃): 7.08-7.16 (6H, m, H3-5), 7.37 (2H, m, H6), 1.26 (9H, d, ^tBu, J(PH) = 13 Hz), 2.33 (6H, s, Me); ³¹P NMR (CDCl₃): -8.7; ¹³C NMR(CDCl₃): 136.5 (19, C1), 143.1 (26, C2), 130.3 (5, C3), 128.0 (C4), 125.1 (C5), 133.4 (C6), 31.2 (14, CMe₃), 28.5 (15, CMe₃), 21.7 (22, Me).
- 8. (2-MeC₆H₄)₂MePO.** ¹H NMR (CDCl₃): 7.18 (2H, dd, H3), 7.40 (2H, t, H4), 7.26 (2H, t, H5), 7.69 (2H, dd, H6), 2.06 (3H, d, PMe, J(PH) = 13 Hz), 2.29 (6H, s, Me); ³¹P NMR (CDCl₃): 31.5; ¹³C NMR (CDCl₃): 131.5 (20, C1), 141.2 (9, C2), 131.7 (7, C3), 131.6 (1, C4), 125.7 (12, C5), 133.0 (C6), 16.8 (74, PMe), 21.1 (4, Me).
- 9. (2-MeC₆H₄)₂^tBuPO.** ¹H NMR (CDCl₃): 7.15-7.18 (4H, m, H3, 5), 7.33 (2H, m, H4), 7.56 (2H, dd, H6), 1.38 (9H, d, ^tBu, J(PH) = 14 Hz), 2.38 (6H, s, Me); ³¹P NMR (CDCl₃): 47.2; ¹³C NMR (CDCl₃): 130.9 (89, C1), 143.4 (6, C2), 131.8 (11, C3), 131.0 (3, C4), 124.6 (12, C5), 132.4 (10, C6), 35.4 (69, CMe₃), 25.9 (CMe₃), 21.5 (4, Me).
- 10. (2-EtC₆H₄)₃PO.** ¹H NMR (CDCl₃): 7.32-7.49 (6H, m, H3, 4), 7.00-7.15 (6H, m, H5, 6), 2.97 (6H, q, CH₂CH₃, J = 7.4 Hz), 1.02 (9H, t, CH₂CH₃); ³¹P NMR (CDCl₃): 34.8; ¹³C NMR (CDCl₃): 131.0 (103, C1), 149.6 (8, C2), 130.0 (11, C3), 131.8 (2, C4), 125.2 (13, C5), 133.0 (12, C6), 27.6 (4, CH₂CH₃), 15.1 (2, CH₂CH₃).
- 11. (2-ⁱPrC₆H₄)₃PO.** ¹H NMR (CDCl₃): 7.10-7.30 (6H, m, H3, 5), 7.45-7.55 (6H, m, H4, 6), 3.65 (3H, m, CHMe₂, J = 6.3 Hz), 1.01 (18H, d, CHMe₂); ³¹P NMR (CD₂Cl₂): 38.2; ¹³C NMR (CDCl₃): 131.1 (102, C1), 154.3 (8, C2), 127.3 (11, C3), 131.9 (3, C4), 125.1 (13, C5), 132.9 (13, C6), 31.3 (4, CHMe₂), 23.9 (CHMe₂).
- 12. (2-MeC₆H₄)₂(2-^tBuC₆H₄)PO.** ¹H NMR (CDCl₃): 6.60 (1H, dd, H6'), 6.87 (1H, dd, H5'), 6.98-7.11 (4H, m), 7.23-7.48 (5H, m), 7.68 (1H, dd, H6'), 2.45, 2.60 (6H, s, Me), 1.54 (9H, s, ^tBu); ³¹P NMR (CDCl₃): 43.4; ¹³C NMR (CDCl₃): 124.6 (14), 124.9 (13), 125.0 (13), 128.0 (11), 129.5 (95), 131.3-132.6 (m), 131.9 (100), 133.3 (13), 134.0 (105), 135.2 (15), 142.7 (7), 144.0 (7), 157.4 (6), 37.6 (2, CMe₃), 32.5 (CMe₃), 21.6, 22.3 (4, Me).
- 13. (2-MeC₆H₄)₂MePS.** ¹H NMR (CDCl₃): 7.14 (2H, t, H3), 7.31-7.42 (4H, m, H4, 5), 8.11 (2H, dd, H6), 2.31 (3H, d, PMe, J(PH) = 13 Hz), 2.09 (6H, s, Me); ³¹P NMR (CDCl₃): 35.1; ¹³C NMR (CDCl₃): 131.6 (79, C1), 140.1 (9, C2), 131.9 (1, C3), 131.7 (3, C4), 126.3 (13, C5), 132.0 (C6), 21.9 (60, PMe), 21.3 (5, Me).

14. (2-MeC₆H₄)₂tBuPS. ¹H NMR (CDCl₃): 7.13 (2H, m(br), H3), 7.23-7.37 (4H, m(br), H4, 5), 7.6-8.5 (2H, m(br), H6), 1.44 (9H, d, ^tBu, J(PH) = 16 Hz), 2.10 (6H, s(br), Me); ³¹P NMR (CDCl₃): 57.3; ¹³C NMR (CDCl₃): 129-135 (br, C1, 3, 4, 6), 142.0 (br, C2), 125.5 (12, C5), 38.0 (60, CMe₃), 26.6 (CMe₃), 22.2 (br, Me).

15. (2-ⁱPrC₆H₄)₃PS. ¹H NMR (CDCl₃): 7.40-7.55 (6H, m, H3, 4), 7.25 (3H, t, H5), 7.78 (3H, m(br), H6), 3.47 (3H, br, CHMe₂), 0.90, (18H, br, CHMe₂); ³¹P NMR (CD₂Cl₂): 45.5; ¹³C NMR(CDCl₃): 130.4 (81, C1), 153.3 (9, C2), 128.1 (10, C3), 131.9 (2, C4), 125.4 (13, C5), 133.1 (br, C6), 31.6 (5, CHMe₂), 23.5 (br, CHMe₂).

16. (2-MeC₆H₄)₂MePSe. ¹H NMR (CDCl₃): 7.08 (2H, t, H3), 7.28-7.37 (4H, m, H4, 5), 8.11 (2H, dd, H6), 2.47 (3H, d, PMe, J(PH) = 13 Hz), 2.03 (6H, s, Me); ³¹P NMR (CDCl₃): 21.3 (J(SeP) = 704 Hz); ¹³C NMR (CDCl₃): 130.0 (71, C1), 140.1 (8, C2), 132.0 (10, C3), 131.8 (3, C4), 126.5 (13, C5), 132.7 (13, C6), 22.4 (53, PMe), 21.2 (5, Me).

17. (2-MeC₆H₄)₂^tBuPSe. ¹H NMR (CDCl₃): 7.0-7.4 (6H, m, H3-5), 7.75 (2H, t, H2), 8.62 (2H, br, H6); ³¹P NMR (CDCl₃): 49.9 (J(SeP) = 696 Hz), ¹³C NMR (CDCl₃): 140.2, 142.7 (br, C2), 131.8, 133.3 (10, 9, C3), 131.1, 131.4 (C4), 125.5, 125.9 (12, 13, C5), 128.8, 136.6 (br, C6), 37.3 (40, CMe₃), 27.0 (CMe₃), 22.2 (4, Me).

18. (2-MeC₆H₄)₂MePCr(CO)₅. ¹H NMR (CDCl₃): 7.18 (2H, m, H3), 7.36-7.40 (4H, m, H4, 5), 7.81 (2H, m, H6), 2.09 (3H, d, PMe, J(P-H) = 6.0 Hz), 1.92 (6H, s, Me); ³¹P NMR (CD₂Cl₂): 37.9; ¹³C NMR(CD₂Cl₂): 134.2 (31, C1), 140.0 (4, C2), 131.5 (6, C3), 129.9 (2, C4), 126.3 (11, C5), 130.7 (17, C6), 17.9 (28, PMe), 20.9 (5, Me), 221.6 (7, CO_{trans}), 216.5 (13, CO_{cis}); Infrared (ν_{max}/cm⁻¹; hexane): 2063, 1949, 1944, 1937.

19. (2-MeC₆H₄)₂^tBuPCr(CO)₅. ¹H NMR (CDCl₃): 7.1-7.3 (6H, m, H3-5), 7.95 (2H, m, H6), 1.30 (9H, d, ^tBu, J(P-H) = 13 Hz), 2.04 (6H, s, Me); ³¹P NMR (CDCl₃): 67.7 (exo₂), 52.3 (exo_{1a}), ¹³C NMR (CDCl₃): 141.8-124.1 (C1-6), 30.2 (br, Me), 23.0 (br, ^tBu), 221.6 (6, CO_{trans}), 216.8 (11, CO_{cis}); infrared: (ν_{max}/cm⁻¹; hexane): 2051, 1971, 1937.

B. FORCE FIELD PARAMETERISATION

Table 1. HF and DFT Geometric and Energetic Comparison for XPH₂R Series (X = lone pair, O, S; R = Me, Bu^t, Ph)

(a) XPH₂Me Series

	PH ₂ Me	OPH ₂ Me	SPH ₂ Me
<i>DFT method</i>			
H-C-P-X rotational barrier/ kJ mol ⁻¹	5.13	6.75	6.95
H-P-H (ground state) ^o	93.3	100.9	100.3
H-P-H (transition state) ^o	92.7	100.8	99.9
H-P-C (ground state) ^o	97.6	102.7	102.1
H-P-C (transition state) ^o	98.1	103.4	102.7
H-C-P-X (ground state) ^o	58*	60	60
H-C-P-X (transition state) ^o	0*	0	0
<i>HF method</i>			
H-C-P-X rotational barrier/ kJ mol ⁻¹	7.25	6.85	7.37
H-P-H (ground state) ^o	92.8	99.4	97.4
H-P-H (transition state) ^o	92.3	99.1	99.9
H-P-C (ground state) ^o	95.7	100.6	98.7
H-P-C (transition state) ^o	96.3	101.4	102.7
H-C-P-X (ground state) ^o	59*	60	60
H-C-P-X (transition state) ^o	0*	0	0

(b) XPH₂Bu^t Series

	PH ₂ Bu ^t	OPH ₂ Bu ^t	SPH ₂ Bu ^t
<i>DFT method</i>			
C-C-P-X rotational barrier/ kJ mol ⁻¹	8.36	10.3	11.1
H-P-H (ground state) ^o	93.4	101.0	100.6
H-P-H (transition state) ^o	92.7	99.1	100.0
H-P-C (ground state) ^o	97.5	102.9	101.8
H-P-C (transition state) ^o	98.3	102.5	102.5
C-C-P-X (ground state) ^o	59*	60	60
C-C-P-X (transition state) ^o	0	0	0
<i>HF method</i>			
C-C-P-X rotational barrier/ kJ mol ⁻¹	11.8	12.0	13.7
H-P-H (ground state) ^o	92.9	99.1	97.6
H-P-H (transition state) ^o	92.1	100.0	97.1
H-P-C (ground state) ^o	95.9	100.8	98.8
H-P-C (transition state) ^o	96.8	99.4	99.4
C-C-P-X (ground state) ^o	59*	60	60
C-C-P-X (transition state) ^o	0*	0	0

(c) XPH₂Ph Series

	PH ₂ Ph	OPH ₂ Ph	SPH ₂ Ph
<i>DFT method</i>			
C _α -C _{ipso} -P-X rotational barrier/ kJ mol ⁻¹	1.19	1.96	1.26
H-P-H (ground state) ^o	93.0	100.7	99.9

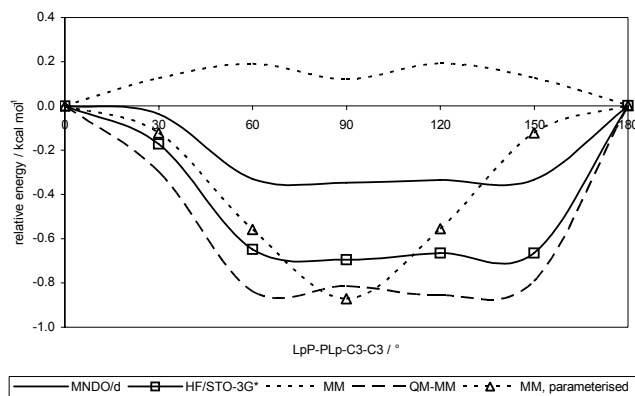
H-P-H (transition state) ^o	93.7	102.4	101.4
H-P-C _{ipso} (ground state) ^o	97.8	103.5	102.4
H-P-C _{ipso} (transition state) ^o	97.3	101.8	101.4
C _α -C _{ipso} -P-X (ground state) ^o	0*	4	4
C _α -C _{ipso} -P-X (transition state) ^o	87*	89	89
HF method			
C _α -C _{ipso} -P-X rotational barrier/ kJ mol ⁻¹	0.740	2.05	1.79
H-P-H (ground state) ^o	93.2	98.8	97.0
H-P-H (transition state) ^o	92.3	99.9	97.9
H-P- C _{ipso} (ground state) ^o	95.9	101.2	99.1
H-P- C _{ipso} (transition state) ^o	95.8	102.7	98.6
C _α -C _{ipso} -P-X (ground state) ^o	88*	0	0
C _α -C _{ipso} -P-X (transition state) ^o	0*	89	90

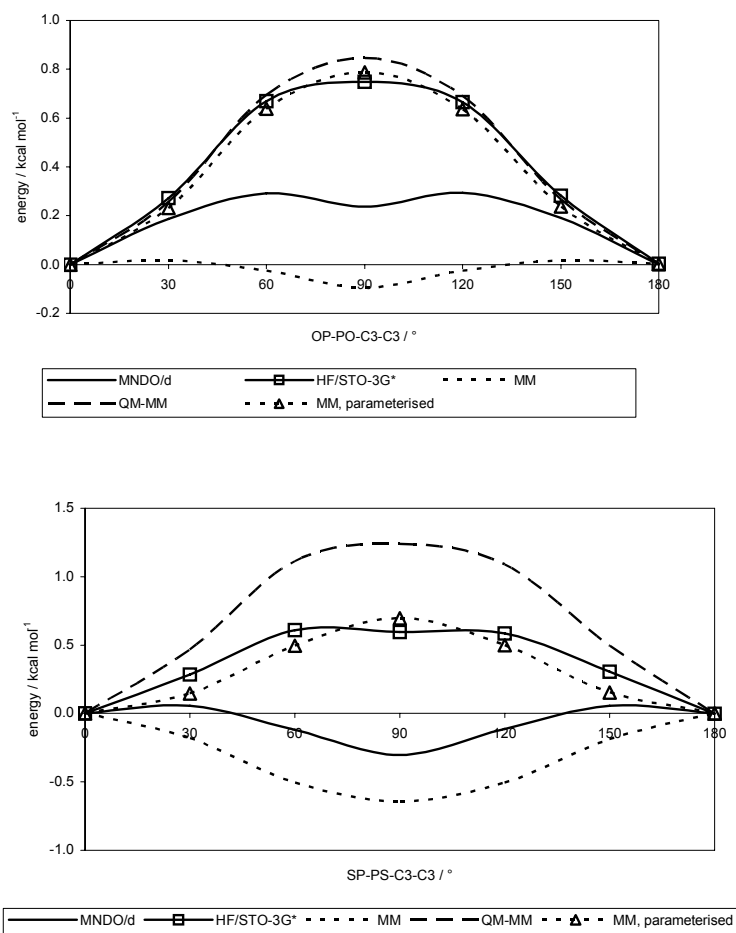
DFT method: calculated using density functional theory with a 6-311G** (d,p) basis set using B3LYP functional

HF method: calculated using Hartree-Fock methods with an STO-3G* basis set

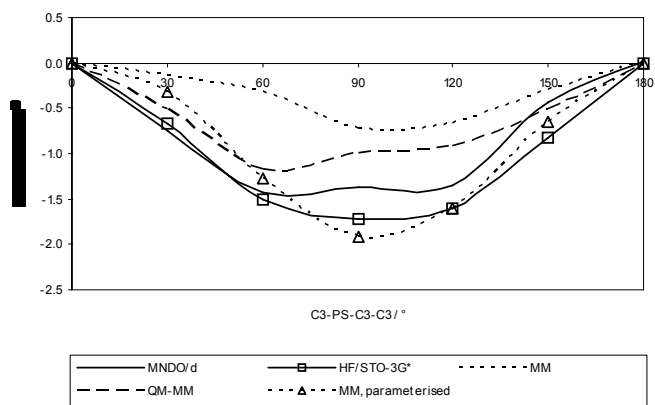
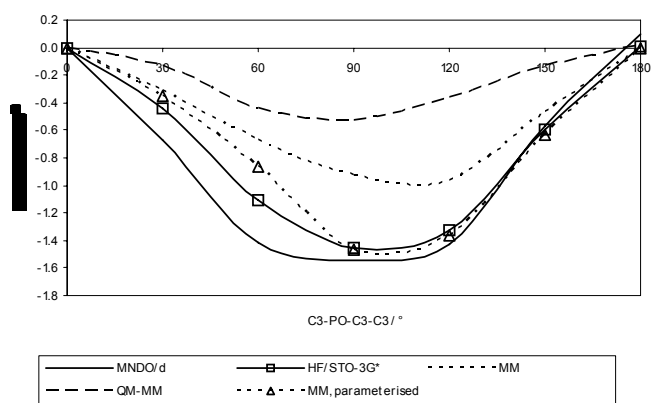
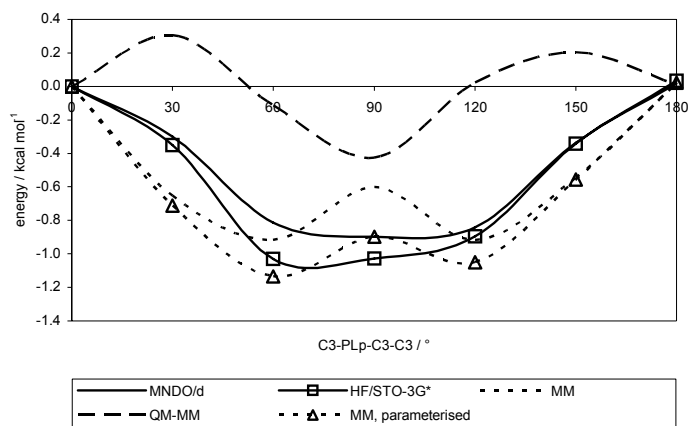
* measured through addition of a hydrogen atom to P to mimic lone pair position

- Phenylphosphine **1a** and its oxide and sulphide **1b, c** were used for parameterisation of the XP-PX-C3-C3 term. It is noteworthy that whereas global minima are observed for the oxide and sulphide with an in-plane conformation (XP-PX-C3-C3 = 0/180 °), the energy minimum for the phosphine itself is perpendicular (XP-PX-C3-C3 = 90 °), implying some conjugative stabilisation in the former.

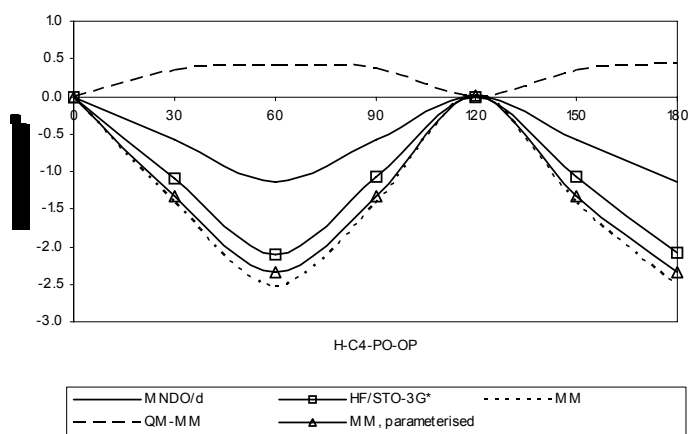
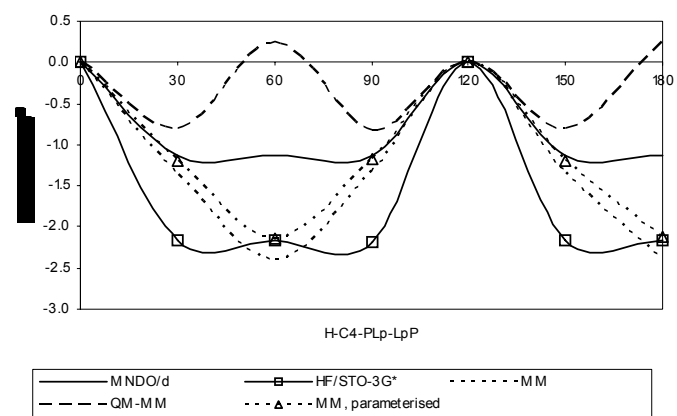


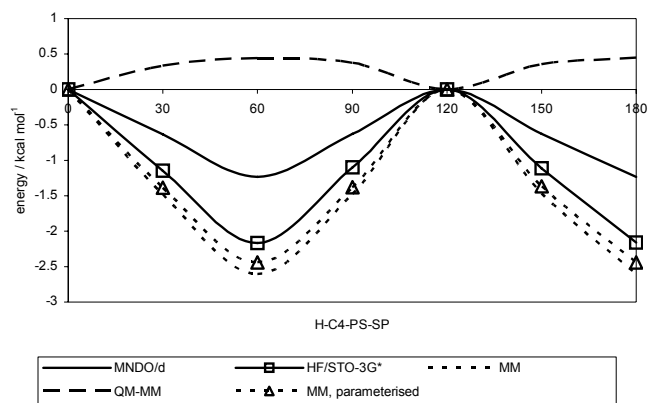


- Diphenylphosphine **2a** and its oxide and sulphide **2b, c** were used for parameterisation of the C3-PX-C3-C3 term. The required torsion to one ring was driven whilst the corresponding torsion to the other ring was allowed to optimise. For the oxide and sulphide, global minima are observed at a perpendicular conformation (C3-PX-C3-C3 = 90 °) rather than a value of 120 °, which would maximise co-planarity of one aryl ring with the X substituent. This perhaps indicates the importance of increased ring-ring and ring-X interactions in determining conformational preference.

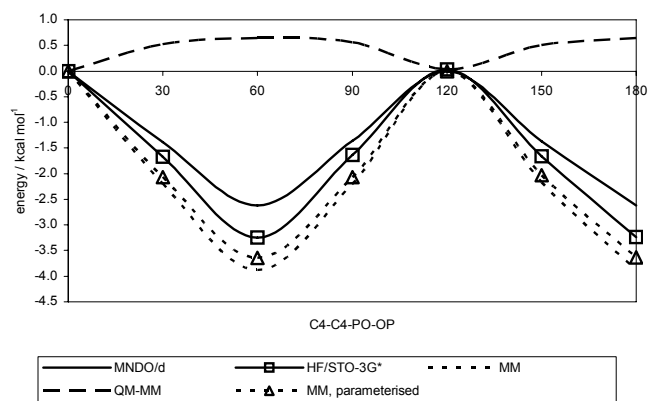
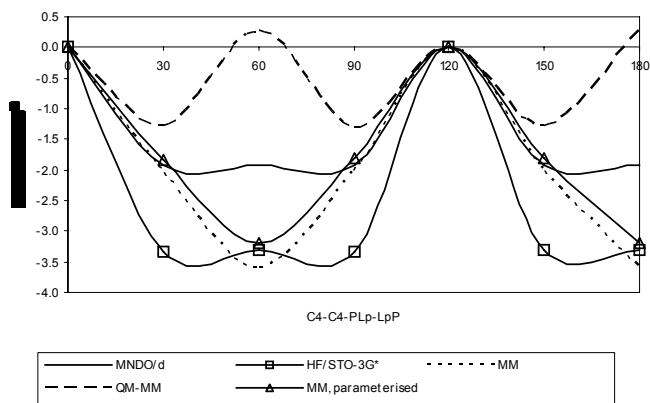


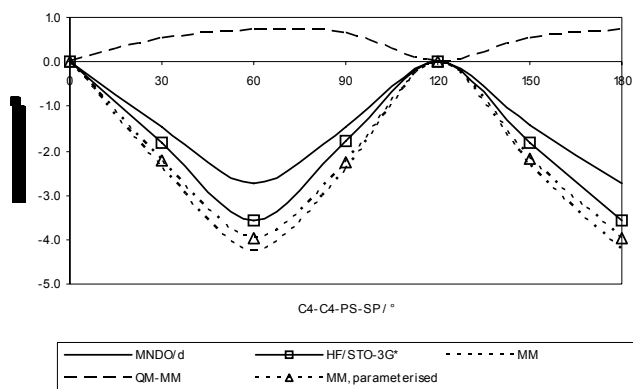
- Methylphosphine **3a** and its oxide and sulphide **3b, c** were used for parameterisation of the H-C4-PX-XP term. As expected, the rotational energy profiles show virtually no dependence on X, giving rise to low V_n values which are similar for all three compounds. All energy profiles show approximate C_3 symmetry. Unusually, the baseline MM profile (H-C4-PX-XP = 0 °) generates a higher rotational barrier than the HF profile.



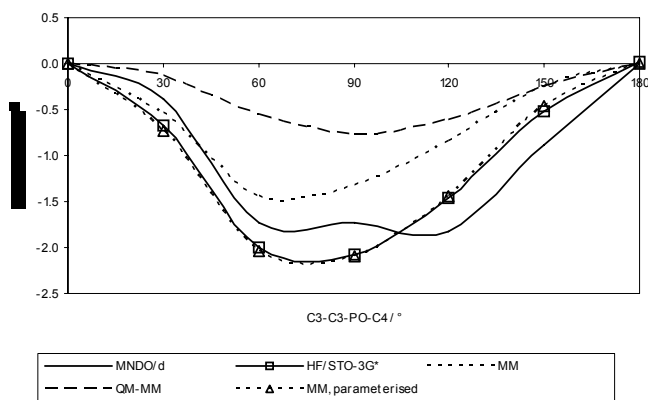
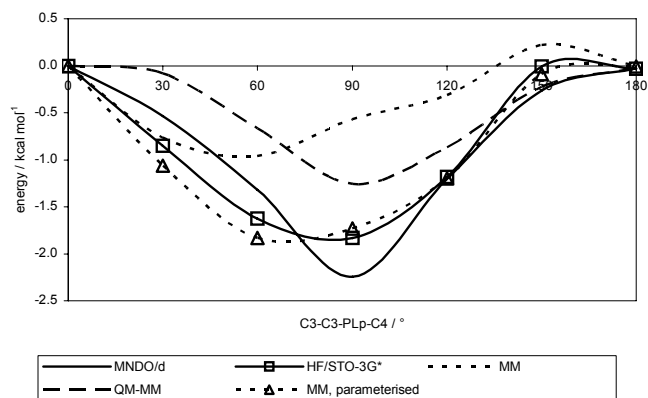


- *tert*-Butylphosphine **4a** and its oxide and sulphide **4b, c** were used for parameterisation of the C4-C4PX-XP term. The profiles are similar to those of **2**, with the expected higher barriers reflected in slightly larger parameters.





- Methylphenylphosphine **5a** and its oxide and sulphide **5b, c** were used for parameterisation of the C3-C3-PX-C4 term. By analogy with **2**, the aryl ring was driven, whilst the methyl group was allowed to adjust freely.



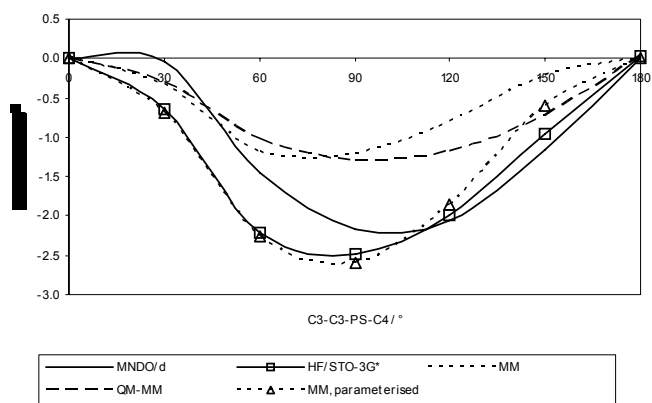


Table 2. Added or Modified Molecular Mechanics Parameters

<i>a) Type</i>		
	Mass / g mol ⁻¹	Description
LpP	0.001	Lone Pair for arylphosphines
OP	15.995	P=O Oxygen for arylphosphines
SP	31.972	P=S Sulphur for arylphosphines
SeP	79.917	P=Se Selenium for arylphosphines
CrP	51.941	Cr (VI) for arylphosphines
PLp	30.994	Lp-P Phosphorus for arylphosphines
PO	30.994	O=P Phosphorus for arylphosphines
PS	30.994	S=P Phosphorus for arylphosphines
PSe	30.994	Se=P Phosphorus for arylphosphines
PCr	30.994	Cr-P Phosphorus for arylphosphines
Cx1, Cx2, Cx3, Cx4	12.000	Cr(CO) ₅ carbon, equatorial
Cx5	12.000	Cr(CO) ₅ carbon, axial
Ox1, Ox2, Ox3, Ox4	15.995	Cr(CO) ₅ oxygen, equatorial
Ox5	15.995	Cr(CO) ₅ oxygen, axial

<i>b) Non-Bonded</i>		
	R* (radius) / Å	ε (well depth) / kcal mol ⁻¹
LpP	1.200	0.016
OP	1.740	0.066
SP	2.110	0.202
SeP	2.250	0.276
CrP	2.210	0.302
PLp, PO, PS, PSe, PCr	2.180	0.168
Cx# (# = 1-5)	1.900	0.044
Ox# (# = 1-5)	1.740	0.066

<i>c) Out-Of-Plane</i>	
	Force constant / mdyn Å rad ⁻²
C3-PX (X=Lp, O, S, Se, Cr)	0.500
PO-OP	0.800
PX-XP (X=S, Se)	0.650

Table 2. Continued

d) Stretching

	Force constant / mdyn Å⁻¹	Equilibrium value / Å	Dipole Moment / Debye
C3-C3	8.065	1.392	0.000
H-PX (X=Lp, O, S, Se) ^a	3.330	1.371	0.500
C3-PLp	4.400	1.820	1.040
C3-PO	4.400	1.800	1.040
C3-PS	4.400	1.800	1.040
C3-PSe	4.400	1.820	1.040
C3-PCr	4.400	1.840	1.040
C4-PLp	2.910	1.860	0.830
C4-PO	2.910	1.830	0.830
C4-PS	2.910	1.810	0.830
C4-PSe	2.910	1.820	0.830
C4-PCr	2.910	1.840	0.830
LpP-PLp	5.000	0.730	0.000
OP-PO	9.000	1.480	-2.567
SP-PS	3.860	1.900	-2.749
SeP-PSe	4.220	2.100	-4.477
CrP-PCr	2.000	2.350	0.000
CrP-Cx# (#=1-4)	5.000	1.860	0.000
CrP-Cx5	5.000	1.820	0.000
Cx1-Ox# (#=1-4)	17.040	1.120	2.600
Cx5-Ox5	17.040	1.150	2.600

^a relevant to model compounds only

Table 2. Continued

e) Bending

	Force constant / mdyn Å rad ⁻²	Equilibrium value / °
C3-PX-H (X=Lp, O) ^a	0.480	100.00
C3-PX-H (X=S, Se) ^a	0.480	101.00
C4-PX-H (X=Lp, O, S, Se) ^a	0.480	100.00
H-PX-H (X=Lp, O, S, Se) ^a	0.438	97.00
H-PLp-LpP*	0.500	120.00
H-PX-XP (X=O, S, Se) ^a	0.650	114.00
C3-PLp-C3	1.500	100.00
C3-PO-C3	1.500	104.00
C3-PX-C3 (X=S, Se)	0.500	104.00
C3-PCr-C3	0.500	100.00
C3-PX-C4 (X=Lp, O)	1.500	103.00
C3-PX-C4 (X=S, Se, Cr)	1.500	104.00
C3-PX-XP (X=Lp, O, X, Se, Cr)	0.500	112.00
C3-PLp-LpP	0.500	110.00
C3-PX-XP (X=O, S)	0.500	113.00
C3-PX-XP (X=Se, Cr)	0.500	111.00
C3-C3-PX (X=Lp, O, S, Se, Cr)	0.380	120.00
C4-C4-PX (X=Lp, O, S, Se, Cr)	0.480	108.00
H-C4-PX (X=Lp, O, S, Se, Cr)	0.360	110.00
PCr-CrP-Cx# (#=1-4)	0.500	90.00
PCr-CrP-Cx5	0.400	180.00
CrP-Cx#-Ox# (#=1-5)	0.500	180.00
Cx1-CrP-Cx2	0.550	90.00
Cx1-CrP-Cx3	0.200	180.00
Cx1-CrP-Cx4	0.550	90.00
Cx1-CrP-Cx5	0.550	90.00
Cx2-CrP-Cx2	0.550	90.00
Cx2-CrP-Cx2	0.200	180.00
Cx2-CrP-Cx2	0.550	90.00
Cx3-CrP-Cx2	0.550	90.00
Cx3-CrP-Cx2	0.550	90.00
Cx4-CrP-Cx2	0.550	90.00

^a relevant to model compounds only

Table 2. Continued

f) Torsions

	$V_1 / \text{kcal mol}^{-1}$	$V_2 / \text{kcal mol}^{-1}$	$V_3 / \text{kcal mol}^{-1}$
C4-C3-C3-C3	-0.270	9.000	0.000
C3-C3-C3-C3	-0.930	4.800	0.000
C4-C3-C3-H	0.000	9.000	0.000
C3-C3-C3-H	0.000	5.405	-1.060
H-C3-C3-H	0.000	9.000	0.000
C3-C3-PX-H (X=Lp, O, S, Se) ^a	0.000	0.000	0.000
C4-C4-PX-H (X=Lp, O, S, Se) ^a	-0.530	-0.400	0.600
H-C4-PX-H (X=Lp, O, S, Se) ^a	0.000	0.000	0.428
C3-C3-C3-PX (X=Lp, O, S, Se, Cr)	0.000	16.250	0.000
C4-C3-C3-PX (X=Lp, O, S, Se, Cr)	-0.100	10.000	0.000
H-C3-C3-PX (X=Lp, O, S, Se, Cr)	0.000	16.250	0.000
H-C4-C4-PX (X=Lp, O, S, Se, Cr)	0.000	0.000	0.330
C4-C4-PX-C3 (X=Lp, O, S, Se, Cr)	-0.500	-0.100	0.300
H-C4-PX-C4 (X=Lp, O, S, Se, Cr)	0.050	0.000	0.200
-PCr-CrP-	0.000	0.000	0.000
PCr-CrP-Cx#-Ox# (# = 1-5)	0.000	0.000	0.000
Ox#-Cx#-PCr-Cx# (# = 1-5)	0.000	0.000	0.000

^a relevant to model compounds only

C. VARIABLE TEMPERATURE NMR LINESHAPE ANALYSES

Copies of the spectra from which these quantities are calculated can be obtained from the corresponding author.

ring exchange (1- or 3- ring flip)					exo ₂ → exo ₃ (minor → major)						
Compound	T/ K	k/ s ⁻¹	ΔG [‡] / kJ mol ⁻¹	ΔH [‡] / kJ mol ⁻¹	ΔS [‡] / J K ⁻¹ mol ⁻¹	Compound	T/ K	k/ s ⁻¹	ΔG [‡] / kJ mol ⁻¹	ΔH [‡] / kJ mol ⁻¹	ΔS [‡] / J K ⁻¹ mol ⁻¹
3a	203	7	45.5 ± 1.7			3b^a	173	900	31.8 ± 0.8		
	213	25	46.0 ± 0.8				183	1600	33.0 ± 0.8		
	223	90	45.5 ± 0.4				193	4500	33.0 ± 0.4		
	233	240	46.0 ± 0.4	46.8 ± 5.0	4.2 ± 20.9		203	7000	34.3 ± 0.8	25.9 ± 3.3	-37.6 ± 16.7
	243	700	46.0 ± 0.8				213	34000	33.0 ± 0.8		
	253	1500	46.4 ± 1.3				223	49000	33.9 ± 1.3		
	268	7000	45.5 ± 1.7				233	80000	34.7 ± 1.3		
							3c	213	13	46.8 ± 0.8	
					223	50		46.8 ± 0.4			
					233	160		46.8 ± 0.4			
					243	450		46.8 ± 0.4			
					253	1150		46.8 ± 0.4			
					263	2800		46.8 ± 0.8	46.8 ± 5.0	0.0 ± 20.9	
					273	5000		47.3 ± 1.3			
					293	30000		46.8 ± 1.7			
4a	203	2	48.1 ± 1.7								
	213	12	47.3 ± 0.8								
	223	55	46.8 ± 0.8								
	233	145	46.8 ± 0.8								
	243	370	47.3 ± 1.3								
	253	920	47.3 ± 1.7								
	263	1920	47.7 ± 2.1								

^a Data for exo₂ → exo₃ ring exchange. ^b Data from ³¹P NMR spectra.

Compound	ring exchange (1- or 3- ring flip)				
	T/ K	k/ s ⁻¹	ΔG^\ddagger / kJ mol ⁻¹	ΔH^\ddagger / kJ mol ⁻¹	ΔS^\ddagger / J K ⁻¹ mol ⁻¹
4b	233	4	53.9 ± 1.3		
	243	20	53.1 ± 0.8		
	253	57	53.1 ± 0.8		
	263	150	53.1 ± 0.8		
	273	340	53.5 ± 1.3	54.4 ± 5.4	4.0 ± 20.9
	283	800	53.5 ± 1.7		
	293	2000	53.1 ± 2.1		
4c	243	95	54.8 ± 2.1		
	253	300	54.8 ± 1.3		
	263	600	55.6 ± 0.8		
	273	1500	55.6 ± 0.4	47.7 ± 7.9	-29.3 ± 29.3
	283	3400	55.6 ± 0.4		
	293	7100	55.6 ± 0.8		
4d	283	7	64.4		
	293	25	64.0		
	303	55	64.0		
	318	180	64.4	64.4	4.18
	333	580	64.4		
	348	1660	64.4		
5a	233	5	53.5 ± 0.8		
	243	16	53.5 ± 0.4		
	253	44	53.5 ± 0.8		
	263	120	53.5 ± 0.8	53.5 ± 5.0	-8.4 ± 20.9
	273	300	53.5 ± 0.8		

Compound	ring exchange (1- or 3- ring flip)					Compound	exo ₂ → exo ₃ (minor → major)				
	T/ K	k/ s ⁻¹	ΔG [‡] / kJ mol ⁻¹	ΔH [‡] / kJ mol ⁻¹	ΔS [‡] / J K ⁻¹ mol ⁻¹		T/ K	k/ s ⁻¹	ΔG [‡] / kJ mol ⁻¹	ΔH [‡] / kJ mol ⁻¹	ΔS [‡] / J K ⁻¹ mol ⁻¹
5b	300	1.3	72.8 ± 1.3			4b^b	173	65	38.9 ± 1.3		
	313	4	73.2 ± 0.8				193	570	39.7 ± 0.8		
	323	10	73.2 ± 0.4				213	5000	39.3 ± 0.4		
	333	23	73.2 ± 0.4				233	2850	39.3 ± 1.3		
	343	55	72.8 ± 0.4				253	140000	38.9 ± 1.7	41.0 ± 5.0	8.4 ± 25.1
	353	110	73.2 ± 0.8	74.0 ± 6.7	4.2 ± 20.9		273	540000	38.9 ± 2.1		
	363	230	73.2 ± 1.3								
						4b	193	33	39.3 ± 0.8		
					203		120	39.3 ± 0.8			
					213		570	38.5 ± 0.8			
					223		1370	38.5 ± 0.8			
					233		3200	38.9 ± 1.3	41.0 ± 5.4	8.4 ± 25.1	
					243		7200	38.9 ± 1.7			
					4c		223	10	49.8 ± 2.1		
							233	30	50.2 ± 0.8		
						243	95	49.8 ± 0.4			
						253	300	49.8 ± 0.4	48.9 ± 5.4	-4.2 ± 20.9	
						263	600	50.2 ± 0.8			
						273	1500	50.2 ± 1.3			
					4d	263	10	59.0			
						273	25	59.4			
						283	65	59.4			
						293	140	59.8			
						303	300	59.8	53.9	-20.9	
						318	850	60.2			

^a Data for exo₂ → exo₃ ring exchange. ^b Data from ³¹P NMR spectra.

Compound	$exo_2 \rightarrow exo_1$					Compound	$exo_2 \rightarrow exo_1$						
	T/ K	k/ s ⁻¹	$\Delta G^\ddagger/$ kJ mol ⁻¹	$\Delta H^\ddagger/$ kJ mol ⁻¹	$\Delta S^\ddagger/$ J K ⁻¹ mol ⁻¹		T/ K	k/ s ⁻¹	$\Delta G^\ddagger/$ kJ mol ⁻¹	$\Delta H^\ddagger/$ kJ mol ⁻¹	$\Delta S^\ddagger/$ J K ⁻¹ mol ⁻¹		
7b	173	370	33.0 ± 0.8	43.9 ± 8.4	58.6 ± 41.8	7e	313	35	67.8 ± 0.4				
	183	1300	33.0 ± 0.4				323	75	68.2 ± 0.4				
	193	6500	32.6 ± 0.8				333	160	67.8 ± 0.8				
	203	37000	31.4 ± 1.3				343	300	67.8 ± 1.3				
					353		700	67.4 ± 2.1					
7c	173	13	38.1 ± 1.3	39.3 ± 7.11	-4.2 ± 33.5	ring exchange							
	183	34	38.9 ± 0.8			Compound	T/ K	k/ s ⁻¹	$\Delta G^\ddagger/$ kJ mol ⁻¹			$\Delta H^\ddagger/$ kJ mol ⁻¹	$\Delta S^\ddagger/$ J K ⁻¹ mol ⁻¹
	193	65	39.7 ± 0.8										
	203	170	40.6 ± 0.4			203	5.0	46.4 ± 0.8					
	213	500	40.6 ± 0.8			213	14	46.8 ± 0.4					
	233	4000	40.6 ± 1.7			223	50	46.8 ± 0.4					
	253	20000	41.0 ± 2.1			233	140	46.8 ± 0.4					
7c^a	183	17	39.8 ± 1.3			243	400	46.8 ± 0.8					
	193	50	40.2 ± 0.8			253	1600	46.0 ± 1.3					
	203	150	40.6 ± 0.4			273	9500	46.0 ± 1.7					
	213	520	40.6 ± 0.4			7c	243	7	55.3 ± 0.8	53.6 ± 4.6	-8.4 ± 16.7		
	223	1600	40.6 ± 0.4				253	20	55.3 ± 0.8				
	233	4200	40.6 ± 0.8			263	60	55.3 ± 0.4					
7d	203	45	42.7 ± 0.8	44.8 ± 6.3	8.4 ± 29.3	273	160	55.3 ± 0.4					
	213	190	42.3 ± 0.4			283	380	55.3 ± 0.4					
	223	450	42.7 ± 0.4			293	8500	55.3 ± 0.8					
	233	1120	43.1 ± 0.4			308	2400	55.7 ± 0.8					
	253	9000	42.7 ± 0.4			323	8000	55.3 ± 1.7					
	273	37000	42.7 ± 0.8			7d	283	7	64.5 ± 0.8	66.1 ± 4.2	8.4 ± 12.6		
7d^a	183	2	43.1 ± 1.7				293	30	63.6 ± 0.4				
	193	8	43.1 ± 1.3										

203	40	42.7 ± 0.8	308	120	63.2 ± 0.4
213	100	43.5 ± 0.8	323	370	63.6 ± 0.4
223	700	41.9 ± 0.8	338	1050	63.6 ± 0.8
233	1500	42.3 ± 0.8	353	2800	63.6 ± 1.3
243	2600	43.1 ± 0.8			
253	8000	42.7 ± 1.3			
263	28000	41.9 ± 1.7			
273	60000	41.9 ± 2.1			

^a Data from ¹H NMR spectra

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