

Supplementary Material

Melem- and melamine-derived iminophosphanes

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Table S1. Crystal structure determination details for compounds **1 - 6**.

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|--|---|---|---|--|---|
| formula | C ₃ Cl ₉ N ₆ P ₃ | C ₄₅ H ₃₈ Br ₂ Cl ₂ N ₆ P ₂ | C ₅₄ H ₅₅ Br ₂ Cl ₃ N ₇ P ₂ | C ₂₀ H ₁₉ Br _{0.79} Cl _{3.21} P | C ₁₂ H ₄ Cl ₁₁ N ₁₀ P ₃ | C ₈ H ₅ Cl ₁₂ N ₁₀ P ₃ |
| M [g / mol] | 532.05 | 955.47 | 1130.16 | 467.14 | 771.11 | 759.53 |
| crystal system | triclinic | monoclinic | triclinic | Cubic | trigonal | monoclinic |
| space group | P-1 | P2 ₁ /n | P-1 | Pa-3 | R3c | P2 ₁ /n |
| cell parameters | | | | | | |
| a [Å] | 10.2641(7) | 13.4575(5) | 14.0193(5) | 16.2023(4) | 18.0719(3) | 14.1973(2) |
| b [Å] | 11.7367(8) | 20.1036(9) | 14.1055(6) | 16.2023(4) | 18.0719(3) | 13.6585(2) |
| c [Å] | 15.4861(11) | 15.6687(6) | 15.1516(6) | 16.2023(4) | 14.7542(6) | 14.7835(3) |
| α [°] | 80.333(3) | 90 | 103.179(2) | 90 | 90 | 90 |
| β [°] | 80.019(3) | 93.930(2) | 96.281(2) | 90 | 90 | 111.938(1) |
| γ [°] | 76.390(3) | 90 | 112.2370(10) | 90 | 120 | 90 |
| V [Å ³] | 1769.9(2) | 4229.1(3) | 2635.91(18) | 4253.34(18) | 4173.1(2) | 2659.14(8) |
| Z | 4 | 4 | 2 | 8 | 6 | 4 |
| ρ _{calcd} [mg / m ³] | 1.997 | 1.501 | 1.424 | 1.459 | 1.841 | 1.897 |
| T [K] | 90(2) | 90(2) | 100(2) | 150(2) | 220(2) | 90(2) |
| λ [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| cryst. size [mm ³] | 0.58 x 0.43 x 0.18 | 0.30 x 0.20 x 0.08 | 0.35 x 0.20 x 0.10 | 0.65 x 0.43 x 0.34 | 0.35 x 0.20 x 0.15 | 0.20 x 0.16 x 0.08 |
| μ [mm ⁻¹] | 1.691 | 2.160 | 1.794 | 2.014 | 1.298 | 1.453 |
| Θ _{max} [°] | 32.00 | 26.00 | 26.00 | 26.98 | 25.97 | 28.00 |
| index range | -15 ≤ h ≤ 15 -17 ≤ k ≤ 17 -23 ≤ l ≤ 22 | -16 ≤ h ≤ 16 -22 ≤ k ≤ 24 -19 ≤ l ≤ 16 | -17 ≤ h ≤ 15 -17 ≤ k ≤ 17 -16 ≤ l ≤ 18 | -17 ≤ h ≤ 20 -20 ≤ k ≤ 20 -20 ≤ l ≤ 18 | -22 ≤ h ≤ 20 -22 ≤ k ≤ 22 -18 ≤ l ≤ 18 | -18 ≤ h ≤ 18 -18 ≤ k ≤ 17 -19 ≤ l ≤ 15 |
| param. / restrain. | 379 / 0 | 526 / 0 | 638 / 21 | 121 / 42 | 127 / 18 | 302 / 0 |
| reflns collected / unique | 48874 / 12204 | 35042 / 8318 | 29620 / 9842 | 23337 / 1557 | 11614 / 1829 | 28179 / 6389 |
| R _{int} | 0.0347 | 0.0507 | 0.0371 | 0.0580 | 0.0338 | 0.0325 |
| absorpt. corr. | | | Semi-empirical from equivalents | | | |
| GoF on F ² | 1.055 | 1.048 | 1.062 | 1.024 | 1.053 | 1.044 |
| R [I > 2σ(I)] | | | | | | |
| R1 | 0.0273 | 0.0418 | 0.0357 | 0.0270 | 0.0296 | 0.0299 |
| wR2 | 0.0625 | 0.0992 | 0.0770 | 0.0544 | 0.0698 | 0.0691 |
| R (all data) | | | | | | |
| R1 | 0.0368 | 0.0735 | 0.0628 | 0.0652 | 0.0364 | 0.0401 |
| wR2 | 0.0649 | 0.1074 | 0.0825 | 0.0637 | 0.0734 | 0.0722 |
| min/max electron density [Å ⁻³] | -0.639 / 0.848 | 0.525 / 1.456 | 0.488 / -0.661 | -0.240 / 0.290 | -0.202 / 0.291 | -0.404 / 0.545 |

Table S2. Bond lengths and angles for compound 4.

| Bond lengths, [Å] | | Bond angles, [°] | |
|-------------------|------------|--------------------|------------|
| Cl(1)-P(1) | 2.0051(13) | C(1)-P(1)-C(1)#1 | 110.59(7) |
| P(1)-C(1) | 1.781(2) | C(1)-P(1)-C(1)#2 | 110.59(7) |
| P(1)-C(1)#1 | 1.781(2) | C(1)#1-P(1)-C(1)#2 | 110.59(7) |
| P(1)-C(1)#2 | 1.781(2) | C(1)-P(1)-Cl(1) | 108.32(8) |
| C(1)-C(6) | 1.382(3) | C(1)#1-P(1)-Cl(1) | 108.32(8) |
| C(1)-C(2) | 1.396(3) | C(1)#2-P(1)-Cl(1) | 108.32(8) |
| C(2)-C(3) | 1.384(3) | C(6)-C(1)-C(2) | 120.2(2) |
| C(3)-C(4) | 1.384(4) | C(6)-C(1)-P(1) | 120.17(19) |
| C(4)-C(5) | 1.377(4) | C(2)-C(1)-P(1) | 119.50(17) |
| C(5)-C(6) | 1.383(4) | C(3)-C(2)-C(1) | 119.7(2) |
| Cl(2)-C(7) | 1.72(3) | C(4)-C(3)-C(2) | 119.6(2) |
| C(7)-C(8) | 1.581(16) | C(5)-C(4)-C(3) | 120.7(2) |
| C(8)-Cl(3) | 1.72(3) | C(4)-C(5)-C(6) | 120.1(2) |
| Cl(4)-C(9) | 1.72(3) | C(1)-C(6)-C(5) | 119.7(2) |
| C(9)-C(10) | 1.581(16) | C(8)-C(7)-Cl(2) | 106(3) |
| C(10)-Cl(5) | 1.72(3) | C(7)-C(8)-Cl(3) | 108(3) |
| | | C(10)-C(9)-Cl(4) | 106(3) |
| | | C(9)-C(10)-Cl(5) | 112(3) |

Quantum chemical analysis

Cartesian coordinates of optimized molecule geometries.

Optimization of **2a**.

| | | | |
|---|-------------|-------------|-------------|
| P | -3.00323000 | -0.09668700 | 0.15516500 |
| P | 3.01413400 | -0.02821400 | 0.12752800 |
| N | -0.01741200 | -0.64595200 | 1.30867700 |
| N | -1.11337900 | -1.71397800 | 3.14421400 |
| H | -2.00989600 | -1.99383000 | 3.52420900 |
| N | 1.14996300 | -1.51021500 | 3.20711100 |
| H | 2.06148600 | -1.64585500 | 3.62820200 |
| N | -2.39343400 | -0.83336400 | 1.50747600 |
| N | 0.05418900 | -2.56893000 | 4.97482900 |
| H | -0.79463800 | -2.89249100 | 5.41692800 |
| H | 0.92217800 | -2.75156800 | 5.45855100 |
| N | 2.36296000 | -0.58808000 | 1.54324000 |
| C | -1.16714300 | -1.01079200 | 1.89194500 |
| C | 0.03137600 | -1.94445900 | 3.79867400 |
| C | 1.15822400 | -0.87322400 | 1.91688700 |
| C | -2.24241800 | -0.60693100 | -1.40916100 |
| C | -1.45030000 | 0.27120600 | -2.16433500 |
| H | -1.25448200 | 1.27794600 | -1.81246100 |
| C | -0.92191500 | -0.15124000 | -3.38432900 |
| H | -0.32456900 | 0.53551500 | -3.97434400 |
| C | -1.16836700 | -1.44421800 | -3.84907000 |
| H | -0.76849600 | -1.76085800 | -4.80734700 |
| C | -1.93771700 | -2.32933400 | -3.08812100 |
| H | -2.13588300 | -3.33292500 | -3.45086000 |
| C | -2.47636500 | -1.91545400 | -1.87181700 |
| H | -3.09676000 | -2.59921800 | -1.30064900 |
| C | -2.92443600 | 1.70787200 | 0.34726300 |
| C | -2.34106000 | 2.28477800 | 1.48343500 |
| H | -1.88161400 | 1.65956100 | 2.24023300 |
| C | -2.37410500 | 3.66887700 | 1.65693400 |
| H | -1.93579700 | 4.11099600 | 2.54617000 |
| C | -2.98524700 | 4.48053500 | 0.70004700 |
| H | -3.01964300 | 5.55601800 | 0.84274500 |
| C | -3.56900000 | 3.90921200 | -0.43389100 |
| H | -4.05424400 | 4.53772500 | -1.17347200 |
| C | -3.54772200 | 2.52773300 | -0.60981000 |
| H | -4.02534600 | 2.09542300 | -1.48361100 |
| C | -4.74143800 | -0.60012300 | 0.11435700 |
| C | -5.41618900 | -0.85911800 | 1.31841700 |
| H | -4.87537800 | -0.83824300 | 2.25760200 |
| C | -6.77796200 | -1.15226300 | 1.30165300 |
| H | -7.29601700 | -1.35741800 | 2.23286300 |
| C | -7.47484500 | -1.18158200 | 0.09157500 |
| H | -8.53573300 | -1.41028500 | 0.08288300 |
| C | -6.80927700 | -0.91869900 | -1.10696600 |

| | | | |
|---|-------------|-------------|-------------|
| H | -7.34897900 | -0.94511900 | -2.04790600 |
| C | -5.44611700 | -0.62640600 | -1.10130200 |
| H | -4.93914800 | -0.43627900 | -2.04151900 |
| C | 3.13222300 | -1.39945300 | -1.04976400 |
| C | 4.38465900 | -1.86742100 | -1.47727900 |
| H | 5.29670800 | -1.40127700 | -1.12149400 |
| C | 4.45607600 | -2.94037800 | -2.36635800 |
| H | 5.42478700 | -3.29932900 | -2.69806900 |
| C | 3.28713400 | -3.54844000 | -2.82414300 |
| H | 3.34696300 | -4.38452800 | -3.51379600 |
| C | 2.03894600 | -3.08357100 | -2.39857100 |
| H | 1.13033200 | -3.55515700 | -2.75803800 |
| C | 1.95357900 | -2.01069800 | -1.51553000 |
| H | 0.98124500 | -1.64998100 | -1.19465200 |
| C | 2.13597600 | 1.35838700 | -0.64016700 |
| C | 1.49673000 | 2.31384000 | 0.16506800 |
| H | 1.44502400 | 2.17884800 | 1.24068100 |
| C | 0.93048300 | 3.44529700 | -0.41846200 |
| H | 0.43120400 | 4.17988700 | 0.20407600 |
| C | 1.01187600 | 3.63711800 | -1.80057100 |
| H | 0.58455700 | 4.52833100 | -2.24939800 |
| C | 1.65128100 | 2.69094900 | -2.60424100 |
| H | 1.72425800 | 2.84520200 | -3.67624200 |
| C | 2.20847000 | 1.54757800 | -2.02983900 |
| H | 2.70074600 | 0.81364300 | -2.65949100 |
| C | 4.66987900 | 0.53047400 | 0.59173100 |
| C | 5.26185100 | 1.62260500 | -0.06310800 |
| H | 4.71654600 | 2.17554100 | -0.82018200 |
| C | 6.55947100 | 2.00983200 | 0.26972800 |
| H | 7.01267000 | 2.85734100 | -0.23381600 |
| C | 7.26901300 | 1.31421900 | 1.24976100 |
| H | 8.27819500 | 1.61978500 | 1.50693200 |
| C | 6.68253000 | 0.22715300 | 1.90333800 |
| H | 7.23502800 | -0.31133300 | 2.66653100 |
| C | 5.38699100 | -0.16756600 | 1.57901100 |
| H | 4.93005800 | -1.00670900 | 2.09158500 |

2b.

| | | | |
|---|-------------|------------|-------------|
| P | 2.83871200 | 0.20355000 | -0.15112100 |
| P | -2.88294600 | 0.25655700 | -0.05317300 |
| N | -0.00508300 | 1.48880900 | -0.58007500 |
| N | 1.17612000 | 3.37236900 | -1.47046100 |
| N | -1.18954300 | 3.50459000 | -1.10060500 |
| N | 2.34693800 | 1.50130600 | -0.91313700 |
| N | -0.00450600 | 5.29501400 | -1.93398600 |
| H | 0.80536000 | 5.57950900 | -2.46230600 |
| H | -0.90065400 | 5.67433400 | -2.19652300 |
| N | -2.34694500 | 1.72978500 | -0.26597000 |

| | | | |
|---|-------------|-------------|-------------|
| C | 1.13039200 | 2.11679600 | -0.98093600 |
| C | -0.00805000 | 3.99806900 | -1.49211200 |
| C | -1.14318900 | 2.23082600 | -0.66245100 |
| C | 2.23009100 | -1.45481800 | -0.66199400 |
| C | 1.23479400 | -2.14082300 | 0.04833200 |
| H | 0.81722600 | -1.71431000 | 0.95331600 |
| C | 0.77354400 | -3.37707400 | -0.40664600 |
| H | 0.00711500 | -3.89897200 | 0.15691600 |
| C | 1.28550600 | -3.93134100 | -1.57987400 |
| H | 0.92400700 | -4.89385200 | -1.93017700 |
| C | 2.25960700 | -3.24319300 | -2.30656700 |
| H | 2.65903700 | -3.66716400 | -3.22331100 |
| C | 2.72971900 | -2.01246200 | -1.85093000 |
| H | 3.49431600 | -1.48803200 | -2.41532700 |
| C | 2.67433600 | 0.28988700 | 1.68050200 |
| C | 2.33314000 | 1.52919800 | 2.23967800 |
| H | 2.11387000 | 2.36745700 | 1.58741500 |
| C | 2.28796300 | 1.68765400 | 3.62540300 |
| H | 2.02355000 | 2.65270400 | 4.04738600 |
| C | 2.58920900 | 0.61367900 | 4.46446500 |
| H | 2.56292500 | 0.74082100 | 5.54302900 |
| C | 2.93011300 | -0.62413800 | 3.91464100 |
| H | 3.16550100 | -1.46320600 | 4.56300700 |
| C | 2.97206100 | -0.78638800 | 2.53014900 |
| H | 3.23052700 | -1.75636200 | 2.11726400 |
| C | 4.64111900 | 0.14601600 | -0.48138000 |
| C | 5.24052700 | 1.24293200 | -1.11334400 |
| H | 4.60802600 | 2.07117700 | -1.41575900 |
| C | 6.61654400 | 1.24679400 | -1.34704300 |
| H | 7.07494600 | 2.09863100 | -1.84087800 |
| C | 7.40059300 | 0.16301900 | -0.94996800 |
| H | 8.47145200 | 0.16908100 | -1.13243800 |
| C | 6.80678800 | -0.93275600 | -0.31932600 |
| H | 7.41249800 | -1.78055200 | -0.01280100 |
| C | 5.43246800 | -0.94243000 | -0.08595500 |
| H | 4.98015400 | -1.80614100 | 0.39188500 |
| C | -2.84609100 | -0.83295900 | -1.53022800 |
| C | -4.00858700 | -1.39356600 | -2.07993500 |
| H | -4.97224300 | -1.21798800 | -1.61407400 |
| C | -3.93346400 | -2.17422600 | -3.23472400 |
| H | -4.83902100 | -2.60394200 | -3.65325200 |
| C | -2.70202200 | -2.39372400 | -3.85231000 |
| H | -2.64642600 | -2.99806500 | -4.75340900 |
| C | -1.54266600 | -1.82989800 | -3.31518000 |
| H | -0.58188000 | -1.99455500 | -3.79303300 |
| C | -1.60850200 | -1.05280100 | -2.15979700 |
| H | -0.71132500 | -0.59826500 | -1.75123700 |
| C | -2.14661700 | -0.73521000 | 1.30855600 |
| C | -1.46187300 | -0.05527100 | 2.32403600 |
| H | -1.32444600 | 1.01806600 | 2.24519000 |
| C | -0.94418900 | -0.75745500 | 3.41267700 |

| | | | |
|---|-------------|-------------|-------------|
| H | -0.39928000 | -0.22556400 | 4.18574800 |
| C | -1.11154600 | -2.14129900 | 3.49770700 |
| H | -0.71073300 | -2.68598600 | 4.34773900 |
| C | -1.78722500 | -2.82643800 | 2.48546700 |
| H | -1.91408500 | -3.90376700 | 2.54658800 |
| C | -2.29548100 | -2.12766200 | 1.38886900 |
| H | -2.79760600 | -2.66802800 | 0.59150600 |
| C | -4.64172500 | 0.47578000 | 0.41083900 |
| C | -5.38958800 | -0.52905400 | 1.04173700 |
| H | -4.92815200 | -1.47594200 | 1.30340200 |
| C | -6.73116100 | -0.31223700 | 1.35730800 |
| H | -7.30226200 | -1.09429900 | 1.84909600 |
| C | -7.33299400 | 0.90984500 | 1.05188900 |
| H | -8.37648100 | 1.07855500 | 1.30237100 |
| C | -6.58927400 | 1.91668300 | 0.43424700 |
| H | -7.05141600 | 2.87237700 | 0.20483700 |
| C | -5.24837400 | 1.70456500 | 0.11383100 |
| H | -4.64522600 | 2.48045000 | -0.34591100 |

cation of **3a**

| | | | |
|---|-------------|-------------|-------------|
| P | 3.82523300 | 0.33357300 | -0.01641900 |
| P | -3.82524900 | 0.33355100 | -0.01634600 |
| N | 0.00000400 | 0.74315100 | -0.10748700 |
| H | -0.00000300 | 1.75156800 | -0.18310500 |
| N | 1.20976100 | -1.25153600 | 0.06013400 |
| N | -1.20969500 | -1.25154800 | 0.06031500 |
| N | -2.28101100 | 0.86462800 | -0.10862000 |
| N | 2.28102400 | 0.86464900 | -0.10893600 |
| H | -0.87082200 | -3.68753200 | 0.06070400 |
| H | 0.87089300 | -3.68754500 | 0.06058700 |
| N | 0.00004100 | -3.19428100 | 0.17176300 |
| C | 1.21311600 | 0.08447900 | -0.04289000 |
| C | 0.00003700 | -1.84770200 | 0.08838200 |
| C | -1.21309500 | 0.08446600 | -0.04272800 |
| C | -4.82685300 | 1.80445500 | -0.37761700 |
| C | -4.26833900 | 3.08329300 | -0.24053800 |
| H | -3.22839800 | 3.18124600 | 0.04827400 |
| C | -5.04834500 | 4.21159900 | -0.49334600 |
| H | -4.61274700 | 5.20051300 | -0.39019400 |
| C | -6.38184600 | 4.07080600 | -0.88063300 |
| H | -6.98530300 | 4.95135400 | -1.07843600 |
| C | -6.94001500 | 2.79821500 | -1.02099100 |
| H | -7.97438600 | 2.68704100 | -1.33031700 |
| C | -6.16680700 | 1.66571000 | -0.77301000 |
| H | -6.60405200 | 0.68001500 | -0.89885300 |
| C | -4.31103500 | -0.28690800 | 1.62787300 |
| C | -5.15982400 | 0.46975800 | 2.45094100 |
| H | -5.56034000 | 1.41514900 | 2.10263900 |
| C | -5.49576600 | 0.00570100 | 3.72291000 |

| | | | |
|---|-------------|-------------|-------------|
| H | -6.15429000 | 0.59533000 | 4.35276500 |
| C | -4.98956600 | -1.21052900 | 4.18101100 |
| H | -5.25475600 | -1.57050400 | 5.17036300 |
| C | -4.14006300 | -1.96507900 | 3.36810400 |
| H | -3.74275700 | -2.90993000 | 3.72592500 |
| C | -3.79699500 | -1.50959100 | 2.09717400 |
| H | -3.12234900 | -2.08282400 | 1.47178700 |
| C | -4.25442400 | -0.92766600 | -1.25982600 |
| C | -5.20129900 | -1.93006500 | -1.00537400 |
| H | -5.66183000 | -2.01415800 | -0.02673200 |
| C | -5.54838500 | -2.83228400 | -2.01261400 |
| H | -6.28162600 | -3.60686700 | -1.81075700 |
| C | -4.95443400 | -2.73956000 | -3.27141200 |
| H | -5.22670200 | -3.44245500 | -4.05272300 |
| C | -4.01055100 | -1.74175400 | -3.52823300 |
| H | -3.54837900 | -1.66827000 | -4.50771000 |
| C | -3.66130100 | -0.83671300 | -2.52906900 |
| H | -2.92772400 | -0.06245700 | -2.73120200 |
| C | 4.82691500 | 1.80460300 | -0.37698600 |
| C | 4.26820900 | 3.08337900 | -0.24018500 |
| H | 3.22809200 | 3.18122600 | 0.04802600 |
| C | 5.04826600 | 4.21176800 | -0.49248900 |
| H | 4.61251800 | 5.20063800 | -0.38954300 |
| C | 6.38200100 | 4.07111100 | -0.87900300 |
| H | 6.98550000 | 4.95171600 | -1.07641800 |
| C | 6.94036300 | 2.79857000 | -1.01909300 |
| H | 7.97492400 | 2.68750700 | -1.32782100 |
| C | 6.16711200 | 1.66599100 | -0.77161400 |
| H | 6.60452000 | 0.68034100 | -0.89725500 |
| C | 4.25466200 | -0.92728100 | -1.26019000 |
| C | 3.66125800 | -0.83636800 | -2.52930300 |
| H | 2.92729000 | -0.06240900 | -2.73114500 |
| C | 4.01073500 | -1.74106700 | -3.52870000 |
| H | 3.54833400 | -1.66762100 | -4.50807100 |
| C | 4.95512400 | -2.73848600 | -3.27224600 |
| H | 5.22756100 | -3.44111600 | -4.05373600 |
| C | 5.54936300 | -2.83116800 | -2.01358100 |
| H | 6.28299300 | -3.60545500 | -1.81200400 |
| C | 5.20205500 | -1.92929000 | -1.00611400 |
| H | 5.66280800 | -2.01335900 | -0.02757200 |
| C | 4.31070000 | -0.28739300 | 1.62770100 |
| C | 5.15836400 | 0.46961600 | 2.45162400 |
| H | 5.55822100 | 1.41554600 | 2.10402800 |
| C | 5.49404500 | 0.00520200 | 3.72352900 |
| H | 6.15169900 | 0.59509700 | 4.35404400 |
| C | 4.98871000 | -1.21173100 | 4.18071900 |
| H | 5.25371300 | -1.57199400 | 5.17001600 |
| C | 4.14031200 | -1.96661900 | 3.36697300 |
| H | 3.74368100 | -2.91202000 | 3.72408700 |
| C | 3.79750200 | -1.51076900 | 2.09610300 |
| H | 3.12367500 | -2.08426000 | 1.47008100 |

cation of **6a**.

| | | | |
|----|-------------|-------------|-------------|
| Cl | -1.39545100 | 6.10089500 | -0.00170200 |
| Cl | -2.92148700 | 3.78502200 | -1.61063200 |
| Cl | -2.92014500 | 3.78739400 | 1.61207700 |
| Cl | 5.86035600 | 0.31015600 | 1.61225300 |
| Cl | 5.86047200 | 0.31109400 | -1.61159200 |
| Cl | 7.12622800 | -2.15702200 | -0.00035000 |
| Cl | -4.83688300 | -4.86706400 | -0.00135300 |
| Cl | -4.79368900 | -2.08624400 | -1.60941100 |
| Cl | -4.79389000 | -2.08856700 | 1.61073900 |
| P | -1.72931400 | 4.12424500 | -0.00003500 |
| P | 5.57841000 | -0.88345900 | -0.00004200 |
| P | -4.02843800 | -3.03731500 | 0.00000500 |
| N | 1.22965600 | 1.75315600 | 0.00026400 |
| N | 2.78173200 | 0.02910200 | 0.00009100 |
| N | 2.03385900 | -2.26050400 | -0.00031000 |
| N | -0.24462500 | -2.68899000 | -0.00028100 |
| H | -0.04096900 | -3.68298800 | -0.00036700 |
| N | -1.86172200 | -0.96761900 | 0.00019700 |
| N | -1.12801600 | 1.23026300 | 0.00020300 |
| N | 0.47293100 | -0.48639800 | -0.00004500 |
| N | -0.32088200 | 3.42553200 | 0.00021800 |
| N | 4.27045400 | -1.77162900 | -0.00032600 |
| N | -2.45861300 | -3.24499900 | 0.00011600 |
| C | -0.06809200 | 2.10181600 | 0.00019700 |
| C | 1.52377900 | 0.46680400 | 0.00010400 |
| C | 3.01467500 | -1.29283100 | -0.00016900 |
| C | 0.81597600 | -1.82608700 | -0.00021600 |
| C | -1.55678400 | -2.25168300 | 0.00000000 |
| C | -0.87055200 | -0.05148300 | 0.00009200 |

5a.

| | | | |
|----|-------------|-------------|-------------|
| Cl | -0.89282600 | -6.78973900 | 0.00000000 |
| Cl | -2.71922900 | -4.70913000 | 1.60805200 |
| Cl | -2.71922900 | -4.70913000 | -1.60805200 |
| Cl | 5.43411100 | -0.00601900 | -1.60805800 |
| Cl | 5.43411100 | -0.00601900 | 1.60805800 |
| Cl | 6.33267900 | 2.61244800 | 0.00000000 |
| Cl | -5.43436500 | 4.17131100 | 0.00000000 |
| Cl | -2.71922900 | 4.71300000 | -1.60777500 |
| Cl | -2.71922900 | 4.71300000 | 1.60777500 |
| P | -1.46200800 | -4.84944700 | 0.00000000 |
| P | 4.93139100 | 1.15487800 | 0.00000000 |
| P | -3.46954600 | 3.69400800 | 0.00000000 |
| N | 1.11074900 | -2.09067300 | 0.00000000 |
| N | 2.35425700 | -0.13396300 | 0.00000000 |
| N | 1.25759000 | 2.00959000 | 0.00000000 |
| N | -1.05881900 | 2.10821200 | 0.00000000 |

| | | | |
|---|-------------|-------------|------------|
| N | -2.36675800 | 0.08647800 | 0.00000000 |
| N | -1.29403800 | -1.96889600 | 0.00000000 |
| N | 0.00045400 | 0.00174900 | 0.00000000 |
| N | -0.15204800 | -4.00178400 | 0.00000000 |
| N | 3.54445500 | 1.87066300 | 0.00000000 |
| N | -3.39024900 | 2.13568500 | 0.00000000 |
| C | -0.11681800 | -2.62867800 | 0.00000000 |
| C | 1.18152400 | -0.76383600 | 0.00000000 |
| C | 2.33716200 | 1.21543500 | 0.00000000 |
| C | 0.07306300 | 1.40746400 | 0.00000000 |
| C | -2.21880700 | 1.41854400 | 0.00000000 |
| C | -1.25315800 | -0.63830400 | 0.00000000 |

Table S3. Comparison between geometries from X-ray structure analyses and optimized geometries.

| molecule | | 2 | 2a | | |
|----------|----|-----------------|--------------------|-----------------------------|---------------------|
| bond | | X-ray structure | optimized geometry | difference | absolute difference |
| P1 | N4 | 1.622 | 1.656 | 0.034 | 0.034 |
| P2 | N6 | 1.609 | 1.656 | 0.047 | 0.047 |
| N1 | C1 | 1.345 | 1.343 | -0.002 | 0.002 |
| N1 | C3 | 1.345 | 1.340 | -0.005 | 0.005 |
| N2 | C2 | 1.336 | 1.338 | 0.002 | 0.002 |
| N2 | C1 | 1.386 | 1.439 | 0.053 | 0.053 |
| N3 | C2 | 1.346 | 1.339 | -0.007 | 0.007 |
| N3 | C3 | 1.388 | 1.437 | 0.049 | 0.049 |
| N4 | C1 | 1.309 | 1.293 | -0.016 | 0.016 |
| N5 | C2 | 1.311 | 1.332 | 0.021 | 0.021 |
| N6 | C3 | 1.307 | 1.297 | -0.01 | 0.010 |
| | | | | Statistical analyses | |
| | | | | Average | 0.022 |
| | | | | Stand.Dev. | 0.020 |
| | | | | Hits | 11 |
| | | | | Lower quartile | 0.006 |
| | | | | Median | 0.016 |
| | | | | Upper quartile | 0.040 |
| | | | | Minimum | 0.002 |
| | | | | Maximum | 0.053 |
| | | | | Range | 0.051 |

Bond lengths to hydrogen atoms are too short from X-ray data. Therefore large deviations are observed. (J. P. Glusker, M. Lewis, M. Rossi, *Crystal Structure Analysis for Chemists and Biologists*, VCH publishers 1994, New York.) Thus the N-H bonds are not considered for statistical analysis but are only listed in the following table.

| molecule | | 2 | 2a | |
|----------|------|-----------------|--------------------|------------|
| bond | | X-ray structure | optimized geometry | difference |
| N2 | H2N | 0.72 | 1.013 | 0.293 |
| N3 | H3N | 0.73 | 1.013 | 0.283 |
| N5 | H5NA | 0.83 | 1.010 | 0.18 |
| N5 | H5NB | 0.9 | 1.010 | 0.11 |

| molecule | | 6 | 6a | | |
|-----------------------------|-----|-----------------|--------------------|------------|---------------------|
| bond | | X-ray structure | optimized geometry | difference | absolute difference |
| P1 | N8 | 1.567 | 1.572 | 0.005 | 0.005 |
| P2 | N9 | 1.5565 | 1.581 | 0.025 | 0.025 |
| P3 | N10 | 1.5602 | 1.583 | 0.023 | 0.023 |
| N1 | C2 | 1.323 | 1.320 | -0.003 | 0.003 |
| N1 | C1 | 1.346 | 1.344 | -0.002 | 0.002 |
| N2 | C2 | 1.333 | 1.332 | -0.001 | 0.001 |
| N2 | C3 | 1.339 | 1.342 | 0.003 | 0.003 |
| N3 | C4 | 1.307 | 1.293 | -0.014 | 0.014 |
| N3 | C3 | 1.367 | 1.378 | 0.011 | 0.011 |
| N4 | C4 | 1.354 | 1.367 | 0.013 | 0.013 |
| N4 | C5 | 1.363 | 1.383 | 0.020 | 0.020 |
| N5 | C5 | 1.326 | 1.320 | -0.006 | 0.006 |
| N5 | C6 | 1.342 | 1.350 | 0.008 | 0.008 |
| N6 | C6 | 1.309 | 1.307 | -0.002 | 0.002 |
| N6 | C1 | 1.36 | 1.372 | 0.012 | 0.012 |
| N7 | C4 | 1.38 | 1.383 | 0.003 | 0.003 |
| N7 | C6 | 1.396 | 1.412 | 0.016 | 0.016 |
| N7 | C2 | 1.4 | 1.419 | 0.019 | 0.019 |
| N8 | C1 | 1.357 | 1.348 | -0.009 | 0.009 |
| N9 | C3 | 1.359 | 1.344 | -0.015 | 0.015 |
| N10 | C5 | 1.345 | 1.342 | -0.003 | 0.003 |
| Statistical analyses | | | | | |
| Average | | | | | 0.010 |
| Stand.Dev. | | | | | 0.007 |
| Hits | | | | | 21 |
| Lower quartile | | | | | 0.003 |
| Median | | | | | 0.009 |
| Upper quartile | | | | | 0.015 |
| Minimum | | | | | 0.001 |
| Maximum | | | | | 0.025 |
| Range | | | | | 0.024 |

Bond lengths to hydrogen atoms are too short from X-ray data. Therefore large deviations are observed. (J. P. Glusker, M. Lewis, M. Rossi, *Crystal Structure Analysis for Chemists and Biologists*, VCH publishers 1994, New York.) Thus the N-H bond is not considered for statistical analysis but is only listed here.

| molecule | | 6 | 6a | |
|----------|-----|-----------------|--------------------|------------|
| bond | | X-ray structure | optimized geometry | difference |
| N4 | H4N | 0.94 | 1.015 | 0.075 |

Table S4: Natural charges at the B3LYP/6-31G(d,p) level.

| atom | 2a | 2b | 3a | difference 2a-2b | difference 3a-2b |
|-------------|-----------|-----------|-----------|-----------------------------|-----------------------------|
| N1 | -0.61 | -0.66 | -0.61 | 0.05 | 0.05 |
| C3 | 0.66 | 0.63 | 0.67 | 0.03 | 0.04 |
| N3 | -0.62 | -0.60 | -0.64 | -0.02 | -0.04 |
| C2 | 0.71 | 0.61 | 0.64 | 0.10 | 0.03 |
| N5 | -0.80 | -0.84 | -0.81 | 0.04 | 0.03 |
| N6 | -0.94 | -1.05 | -1.00 | 0.11 | 0.05 |
| P2 | 1.92 | 1.91 | 1.91 | 0.01 | 0.00 |

| atom | 6a | 5a | difference 6a-5a |
|--------------|-----------|-----------|-----------------------------|
| N7 | -0.47 | -0.47 | 0.00 |
| C4 | 0.67 | 0.65 | 0.02 |
| N4 | -0.60 | -0.52 | -0.08 |
| C5 | 0.66 | 0.62 | 0.04 |
| N5 | -0.56 | -0.58 | 0.02 |
| C6 | 0.66 | 0.65 | 0.01 |
| N10 | -1.00 | -0.98 | -0.02 |
| P3 | 1.53 | 1.54 | 0.01 |
| Cl7 | -0.12 | -0.18 | 0.06 |
| Cl8 | -0.15 | -0.20 | 0.05 |
| Cl9 | -0.15 | -0.20 | 0.05 |
| Cl (average) | -0.14 | -0.19 | 0.05 |