

Structure of 1-Anilino-4-*tert*-butyl-1 λ^5 -phosphorinane 1-Oxide

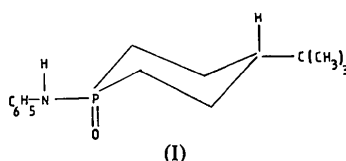
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Abstract. $C_{15}H_{24}NOP$, $M_r = 265.34$, orthorhombic, $Pbca$, $a = 10.140$ (3), $b = 29.035$ (2), $c = 10.203$ (1) Å, $V = 3003.91$ Å³, $Z = 8$, $D_x = 1.18$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 15.14$ cm⁻¹, $F(000) = 1152$, $T = 298$ K, $R = 0.0452$ for 1959 observed reflections. The heterocyclic ring has a chair conformation with slight flattening at the phosphorus end to relieve steric strain. The aniline and *tert*-butyl groups are *trans* to each other and in the equatorial positions. An N...O hydrogen bond results in dimer formation [N...O 2.87 (3) Å, N—H...O 171 (3)°].

Introduction. The stereochemistry of a phosphorinane oxide was reported recently by Macdonell, Berlin, Baker, Ealick, van der Helm & Marsi (1978), and that of a phosphorinane sulfide by Quin, McPhail, Lee & Onan (1974). In each case the phosphorinane ring assumes a chair conformation, flattened at the phosphorus end relative to that of cyclohexane. It is observed that the positioning of the larger substituent on P is important in determining the extent of the flattening. We now report the X-ray crystallographic results for a second phosphorinane oxide (I) which supports the above findings.



Experimental. Crystal ca $0.20 \times 0.30 \times 0.80$ mm grown from chloroform. Accurate cell dimensions from least-squares refinement of 25 high-order reflections in $27 < \theta < 34^\circ$ range. Intensity data collected on Enraf-Nonius CAD-4 diffractometer, take-off angle 5° , Cu $K\alpha$ radiation, graphite-crystal-monochromatized, ω - 2θ scan technique, hkl range: $0 < h < 11$, $0 < k < 32$, $0 < l < 11$; total 2702 reflections measured up to $\theta = 60^\circ$; 2233 unique with $R_{int} = 0.0207$; 1959 observed with $I > 3\sigma(I)$; no significant intensity change for three control reflections after every 9000 s. Corrections for L_p effects applied; no absorption corrections made,

extinction corrections minimized R value significantly with final extinction parameter $x = 3.48 \times 10^{-3}$. Structure solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by least-squares procedure *SHELX76* (Sheldrick, 1976) using F values with weights derived from counting statistics; non-H atoms refined anisotropically; H-atom positions taken from difference map and refined isotropically. Weighting scheme of the form $w = 1.0/(\sigma^2 |F_o| + gF_o^2)$ employed with final $g = 4.327 \times 10^{-3}$ to minimize $\sum w\Delta F^2$, final $R = 0.0452$, $wR = 0.0563$; max. shift e.s.d. = 0.091, largest peak = 0.32 e Å⁻³; $S = 1.17$. Form factors for non-H atoms from Cromer & Mann (1968); for H atoms from Stewart, Davidson & Simpson (1965). Calculations on IBM 3033 computer of the University of Petroleum and Minerals.

Discussion. Fig. 1 is an *ORTEP* diagram (Johnson, 1976) of the molecule illustrating 30% probability ellipsoids for the non-H atoms and arbitrary spheres of radius 0.1 Å for the H atoms. It also shows the conformation and numbering scheme. Fig. 2 shows the packing of the molecules in the unit cell. Table 1 lists the final fractional atomic coordinates and Table 2 contains the bond lengths and angles involving non-H atoms together with selected torsion angles for the title compound.†

† Lists of coordinates, bond lengths and angles involving H atoms, together with structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42410 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

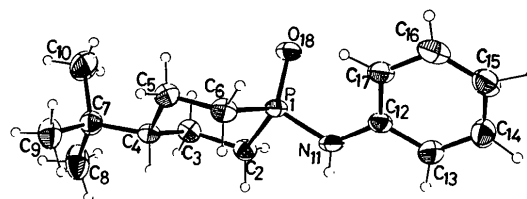


Fig. 1. *ORTEP* diagram of the $C_{15}H_{24}NOP$ molecule.

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The heterocyclic ring in 1-anilino-4-*tert*-butylphosphorinane 1-oxide adopts a chair conformation similar to that of cyclohexane, but with slight flattening at the phosphorus end (the relevant torsion angles are reported in Table 2). The *tert*-butyl and aniline groups are *trans* to each other and occupy equatorial positions on the phosphorinane ring. The chair conformation in this compound has similar angles to those of *trans*-4-*tert*-butyl-1-phenylphosphorinane 1-oxide (Macdonell *et al.*, 1978). Thus the torsion angle C(6)–P(1)–C(2)–C(3) of 53.2 (4)° compares well with the value of 54.7° in the latter compound, and this angle, as expected, is larger than the mean value of *ca* 45° found for cases in which a bulky substituent on P is axially oriented with respect to the ring (Quin, 1980). The diminution in angle under these circumstances is a direct result of ring flattening induced as a mechanism to relieve steric strain.

The P(1)–C(2) and P(1)–C(6) distances [1.782 (2) and 1.795 (2) Å] are significantly shorter than a 'normal' P–C bond of 1.872 Å but are similar to the values of 1.791 (2) and 1.795 (2) Å reported for *trans*-4-*tert*-butyl-1-phenylphosphorinane 1-oxide by Macdonell *et al.* (1978). The P(1)–O(18) distance of 1.478 (2) Å is not significantly different from the 1.483 Å found in the above compound or the average value of 1.462 Å reported by Corbridge (1974) for a large sample of compounds containing highly electronegative atoms attached to a P atom. The average distance in the aniline group is 1.383 (3) Å and the average angle 120.0 (2)°.

An examination of intermolecular distances indicates that the crystal structure is built up of C₁₅H₂₄NOP units linked into dimers by N...O hydrogen bonds [the N...O distance being 2.87 (3) Å and N–H...O angle 171 (3)°]. All other intermolecular contacts are of the normal van der Waals type.

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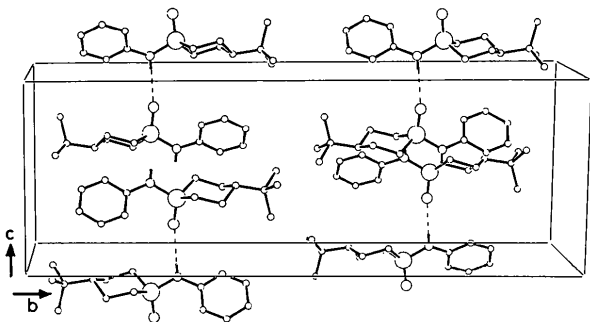


Fig. 2. The unit cell for the C₁₅H₂₄NOP molecules, showing the hydrogen bonding.

Table 1. Fractional atomic positions ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for the non-H atoms; the *e.s.d.*'s are in parentheses

| | $U_{eq} = \frac{1}{3}(\text{trace of orthogonalized } U_{ij} \text{ matrix}).$ | | | |
|-------|--|------------|------------|----------|
| | x | y | z | U_{eq} |
| P(1) | 2186.5 (5) | 2261.7 (2) | 6363.3 (5) | 46 |
| C(2) | 1018 (2) | 1919 (1) | 5496 (2) | 54 |
| C(3) | 1097 (2) | 1416 (1) | 5927 (2) | 55 |
| C(4) | 2443 (2) | 1192 (1) | 5662 (2) | 49 |
| C(5) | 3531 (2) | 1442 (1) | 6430 (2) | 57 |
| C(6) | 3688 (2) | 1951 (1) | 6068 (2) | 57 |
| C(7) | 2460 (2) | 662 (1) | 5896 (3) | 61 |
| C(8) | 1399 (3) | 434 (1) | 5043 (5) | 98 |
| C(9) | 3776 (3) | 457 (1) | 5435 (4) | 84 |
| C(10) | 2266 (6) | 538 (1) | 7326 (4) | 104 |
| N(11) | 2213 (2) | 2754 (1) | 5562 (2) | 59 |
| C(12) | 2710 (2) | 3178 (1) | 5999 (2) | 49 |
| C(13) | 2271 (2) | 3578 (1) | 5398 (2) | 63 |
| C(14) | 2737 (3) | 4004 (1) | 5801 (3) | 80 |
| C(15) | 3633 (3) | 4037 (1) | 6796 (3) | 81 |
| C(16) | 4092 (3) | 3641 (1) | 7392 (2) | 73 |
| C(17) | 3626 (2) | 3212 (1) | 7002 (2) | 58 |
| O(18) | 1896 (2) | 2318.1 (5) | 7773 (1) | 63 |

Table 2. Molecular geometry; *e.s.d.*'s are in parentheses

| (a) Distances (Å) | | | |
|---------------------------------|-----------|---------------------|-----------|
| C(2)–P(1) | 1.782 (2) | C(9)–C(7) | 1.535 (4) |
| C(6)–P(1) | 1.795 (2) | C(10)–C(7) | 1.516 (5) |
| N(11)–P(1) | 1.648 (2) | C(12)–N(11) | 1.403 (3) |
| O(18)–P(1) | 1.478 (2) | C(13)–C(12) | 1.387 (3) |
| C(3)–C(2) | 1.527 (3) | C(17)–C(12) | 1.386 (3) |
| C(4)–C(3) | 1.536 (3) | C(14)–C(13) | 1.385 (4) |
| C(5)–C(4) | 1.534 (3) | C(15)–C(14) | 1.366 (4) |
| C(7)–C(4) | 1.557 (3) | C(16)–C(15) | 1.384 (4) |
| C(6)–C(5) | 1.533 (3) | C(17)–C(16) | 1.389 (3) |
| C(8)–C(7) | 1.535 (4) | | |
| (b) Angles (°) | | | |
| C(2)–P(1)–O(18) | 114.4 (1) | C(8)–C(7)–C(10) | 110.6 (3) |
| C(2)–P(1)–N(11) | 104.4 (1) | C(9)–C(7)–C(4) | 110.3 (2) |
| C(6)–P(1)–C(2) | 101.5 (1) | C(9)–C(7)–C(8) | 105.5 (2) |
| C(6)–P(1)–N(11) | 109.8 (1) | C(9)–C(7)–C(10) | 108.3 (3) |
| C(6)–P(1)–O(18) | 112.9 (1) | C(10)–C(7)–C(4) | 112.4 (2) |
| N(11)–P(1)–O(18) | 113.0 (1) | C(12)–N(11)–P(1) | 127.6 (2) |
| C(3)–C(2)–P(1) | 110.9 (1) | C(13)–C(12)–N(11) | 118.6 (2) |
| C(4)–C(3)–C(2) | 113.6 (2) | C(17)–C(12)–N(11) | 122.5 (2) |
| C(5)–C(4)–C(3) | 110.4 (2) | C(17)–C(12)–C(13) | 118.8 (2) |
| C(7)–C(4)–C(3) | 113.7 (2) | C(14)–C(13)–C(12) | 120.4 (3) |
| C(7)–C(4)–C(5) | 112.4 (2) | C(15)–C(14)–C(13) | 120.8 (3) |
| C(6)–C(5)–C(4) | 114.0 (2) | C(16)–C(15)–C(14) | 119.4 (2) |
| C(5)–C(6)–P(1) | 110.9 (1) | C(17)–C(16)–C(15) | 120.4 (2) |
| C(8)–C(7)–C(4) | 109.5 (2) | C(16)–C(17)–C(15) | 120.2 (2) |
| (c) Selected torsion angles (°) | | | |
| P(1)–C(2)–C(3)–C(4) | –61.4 (3) | C(4)–C(5)–C(6)–P(1) | 59.6 (3) |
| C(2)–C(3)–C(4)–C(5) | 61.7 (4) | C(5)–C(6)–P(1)–C(2) | –52.3 (3) |
| C(3)–C(4)–C(5)–C(6) | –60.9 (4) | C(6)–P(1)–C(2)–C(3) | 53.2 (4) |

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The Structure of Tetramethylammonium Undecahydro(triethylamine)- [I_h-(1551)-Δ²⁰-closo]dodecaborate(1-)*

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Abstract. C₄H₁₂N⁺.C₆H₂₆B₁₂N⁻, *M_r* = 316.15, monoclinic, *P*2₁/*c*, *a* = 10.620 (4), *b* = 14.558 (5), *c* = 13.244 (4) Å, β = 90.40 (3)°, *U* = 2047.6 Å³, *Z* = 4 ion pairs, *D_x* = 1.025 Mg m⁻³, Mo *K*α, λ = 0.71093 Å, μ = 0.047 mm⁻¹, *F*(000) = 688, *T* = 295 K, final *R* = 0.0695 for 965 observed reflections. [NMe₄][Et₃NB₁₂H₁₁] forms as well separated ion pairs. In the anion the B₁₂ fragment is not significantly distorted from an icosahedral geometry, and the B–N bond length, 1.632 (11) Å, compares favourably with that found in the previously studied potassium salt. The B₁₂ framework is less distorted than that in the potassium salt.

Introduction. There has recently been some controversy concerning the relative importance of radial (cross-polyhedral) versus tangential B–B bonding in the series of closo-borane dianions [B_nH_n]²⁻ (Fuller & Keppert, 1984; Housecroft & Wade, 1983). One potential method of quantifying the electron densities associated with these two kinds of interaction is through a series of deformation density studies.

In attempting to synthesize [NMe₄]₂[B₁₂H₁₂] for this purpose we have serendipitously isolated a small amount of the compound [NMe₄][Et₃NB₁₂H₁₁], characterized by the single-crystal X-ray diffraction study described herein. Shortly after completion of this work we became aware that the synthesis of [NMe₄][Et₃NB₁₂H₁₁] had previously been reported, as had a crystallographic study of the potassium salt (Agafonov, Butman, Solntsev, Vinokurov, Zhukova & Kuznetsov, 1982).

Experimental. To the solid product of an attempted synthesis of [HNEt₃]₂[B₁₂H₁₂], prepared according to Miller & Muettteries (1967) but at somewhat reduced temperature (448 K), was added, dropwise, 0.2*M* NaOH with constant boiling. The resulting solution was cooled to room temperature, and an excess of aqueous [NMe₄]Cl was added. On cooling to 276 K colourless crystals were deposited, which were collected, washed with cold water and recrystallized by slow evaporation of a solution in 2-methoxyethanol:water, 1:1. Clear colourless blocks, 0.03 × 0.02 × 0.02 cm, mounted on a glass fibre; preliminary Weissenberg photography; CAD-4 diffractometer; lattice parameters from 25 centred reflections, 9 < θ < 12°; graphite-monochromated Mo *K*α; for data collection θ_{max} = 20°; ω–2θ scan in 96 steps; ω-scan width (0.8 + 0.35 tanθ)°, rapid prescan, following which reflections with *I* ≥ 0.33σ(*I*) remeasured such that final net intensity had *I* ≥ 50σ(*I*), subject to a maximum measuring time of 100 s; no significant crystal movement or decay; 2039 data measured (*h* 0→10, *k* 0→14, *l* –12→12) over ca 53 h. X-ray exposure yielding 1902 unique data on merging (*R*_{int} = 0.0361); for structure solution and refinement 967 amplitudes used [*F* ≥ 2.0σ(*F*)]; automatic direct methods (Sheldrick, 1984) and iterative refinement/Δ*F* syntheses (Sheldrick, 1976); full-matrix least squares (*F*); *w*⁻¹ = [σ²(*F*) + 0.00268(*F*)²]; anisotropic thermal parameters for all non-H atoms; borane H atoms located from Δ*F* synthesis and positionally refined; methylene H atoms set in idealized positions, allowed to ride on respective C atoms; methyl functions treated as rigid groups allowed full rotation about C atom pivots, with chemical sense of resulting C–C–H angles checked; all

* Nomenclature according to Casey, Evans & Powell (1983).