

Fig. 4. Stereoscopic drawing of molecular packing of (I) in the unit cell. Dashed lines represent the intermolecular hydrogen bonds.

C—C—H and H—C—H bond angles are within reasonable ranges of magnitudes. The O—H bond length of the hydroxy group is 0.79 (3) Å, and there is an intermolecular hydrogen bond which links the hydroxy group to the phosphine oxide, as shown in the molecular packing diagram in Fig. 4. The hydrogen-bond distance $O(2)\cdots O(P)(1-x, -y, 1-z)$ is 2.707 (2) Å, and the angle $O(2)-H(O2)\cdots O(P)$ is 174 (3)°. There are no other intermolecular contacts shorter than van der Waals interactions. The closest

contacts involving non-hydrogen atoms are 3.485 (2) and 3.387 (3) Å for $C(1)\cdots O(P)$ and $C(2)\cdots O(P)$ respectively.

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Structure of 1-Azacarbazole, $C_{11}H_8N_2$

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Abstract. $M_r = 168.20$, monoclinic, $P2_1/n$, $a = 11.318$ (2), $b = 5.547$ (1), $c = 13.516$ (6) Å, $\beta = 95.71$ (2)°, $V = 844.3$ (4) Å³, $Z = 4$, $D_x = 1.32$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54187$ Å, $\mu = 5.5$ cm⁻¹, $F(000) = 352$, room temperature, final $R = 0.055$ for 1160 observed reflections. The molecules form hydrogen-bonded dimers [$N\cdots N' = 2.946$ (2) Å] in centrosymmetrically related pairs. The ring system deviates significantly from planarity, maximum atomic deviations -0.039 (2) and $+0.046$ (2) Å.

Introduction. Waluk, Grabowska, Pakuła & Sepiół (1984) and Waluk & Pakuła (1984) suggested that 1-azacarbazole dimers undergo tautomerization in excited states *via* co-operative two-proton transfer between the monomeric units. For photochemical study it is important to know the geometry of the azacarbazole molecules and this study was therefore undertaken in order to establish in particular whether the

azacarbazole molecules exist as planar or distorted dimers.

Experimental. Crystal dimensions 0.2 × 0.2 × 0.3 mm; accurate cell dimensions by least squares from setting angles of 20 reflections; Siemens AED diffractometer, monochromated Cu $K\alpha$ radiation; 1871 reflections with $3 \leq \theta \leq 70^\circ$ measured; $\omega-2\theta$ scans; reference reflection 212 measured periodically during data collection exhibited no significant decrease in intensity; intensities corrected for Lorentz and polarization factors but not for absorption or extinction.

Structure solved by direct methods with *SHELX76* (Sheldrick, 1976). All non-H atoms located in best *E* map. Subsequent refinement based on 1160 observed reflections above threshold [$I_o \geq 2\sigma(I_o)$]; index range $h \pm 13$, $k 0/6$, $l 0/16$. All H atoms, except for H(9) which was located in a difference Fourier map, introduced in calculated positions [$d(\text{C}-\text{H} = 1.08$ Å).

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$)

	x	y	z	U_{eq}
N(1)	1226 (1)	2817 (3)	4623 (1)	506
C(2)	1956 (2)	1417 (4)	4152 (2)	570
C(3)	2492 (2)	-656 (4)	4551 (2)	631
C(4)	2268 (2)	-1436 (4)	5488 (2)	548
C(5)	1513 (2)	-67 (3)	5998 (1)	441
C(6)	1035 (2)	2048 (3)	5529 (1)	435
C(7)	1033 (2)	-204 (3)	6948 (1)	446
C(8)	298 (2)	1845 (3)	6996 (1)	452
N(9)	324 (2)	3193 (3)	6140 (1)	506
C(10)	1120 (2)	-1854 (4)	7721 (2)	547
C(11)	490 (2)	-1457 (4)	8526 (2)	622
C(12)	-236 (2)	570 (4)	8570 (2)	602
C(13)	-338 (2)	2247 (4)	7809 (2)	558

E.s.d.'s are given in parentheses. $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

Full-matrix least-squares anisotropic refinement of non-H atoms and isotropic refinement of H atoms, R magnitudes, final $R = 0.055$, $wR = 0.058$, $w = 1/[\sigma^2(F) + 0.011F^2]$. Max. shift-to-error ratio 0.14 and in final difference map maximum electron density ranged from -0.30 to 0.25 e \AA^{-3} . Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic parameters are in Table 1.*

The bond distances and valence angles together with the numbering of atoms are shown in Fig. 1. Comparison of these data with those found in carbazole (Kurahashi, Fukuyo, Shimada, Furusaki & Nitta, 1969) reveals some significant differences at the 4σ level. Apart from obvious differences due to the presence of the N(1) nitrogen, the bond C(5)–C(7) is shortened by 0.023 \AA in 1-azacarbazole.

The molecule as a whole deviates significantly from planarity with N(1) and N(9) deviating in opposite directions by $0.028 (2)$ and $-0.039 (2) \text{ \AA}$ respectively from the mean molecular plane. If we define three least-squares planes of the individual rings as (I) [N(1), C(2)–C(6)], (II) [C(8), C(7), C(10)–C(13)] and (III) [N(9), C(6), C(5), C(7), C(8)], then the respective dihedral angles are: (I)–(II) $3.3 (1)$, (I)–(III) $1.3 (1)$ and (II)–(III) $2.1 (1)^\circ$.

The azacarbazole molecules are assembled in the crystal pairwise (Fig. 2). The members of each pair are related to each other by a centre of symmetry and are linked by two hydrogen bonds: N(9)–H(9)···N(1') and N(9')–H(9')···N(1) with an N(9)···N(1') distance of $2.946 (2) \text{ \AA}$ (prime denotes equivalent position $-x, 1-y, 1-z$). The distance between the planes defined by the two monomeric units is $0.30 (1) \text{ \AA}$.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42086 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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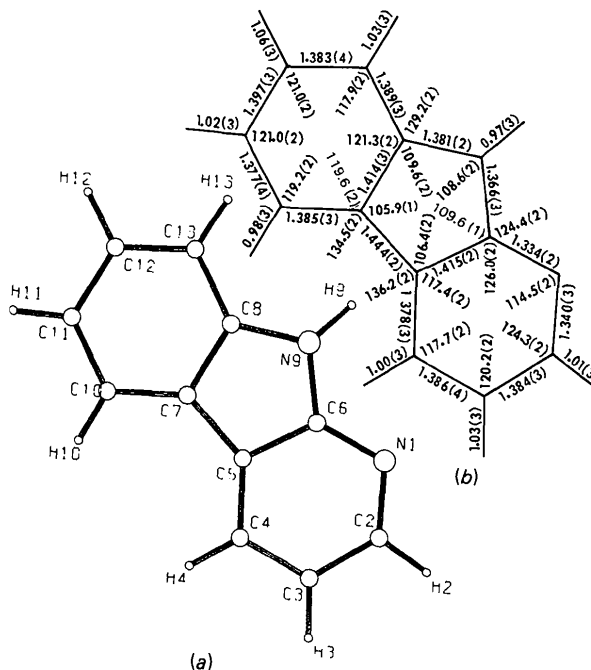


Fig. 1. (a) Atom numbering and (b) bond distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses.

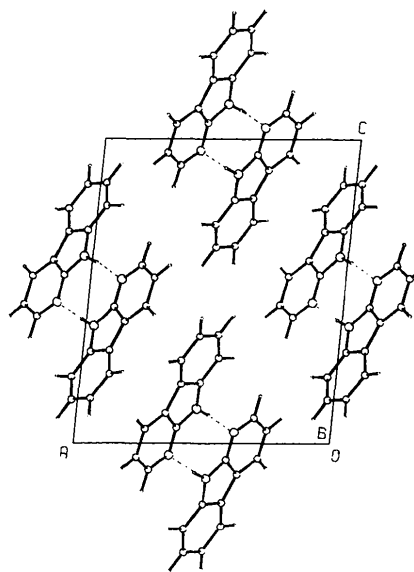


Fig. 2. Molecular packing and hydrogen-bonding scheme as viewed along b , drawn with *PLUTO74* (Motherwell, 1974).

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Structure of 2,2,3,4,4-Pentamethyl-1-(1-naphthyl)- λ^5 -phosphetane 1-Oxide, C₁₈H₂₃OP

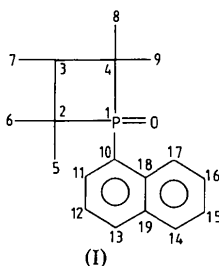
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Abstract. $M_r = 286.36$, orthorhombic, $P2_12_12_1$, $a = 8.009$ (2), $b = 12.195$ (8), $c = 16.425$ (9) Å, $V = 1604.22$ Å³, $Z = 4$, $D_x = 1.19$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å, $\mu = 14.38$ cm⁻¹, $F(000) = 616.00$, $T = 298$ K, $R = 0.0345$ for 1575 observed reflections. The four-membered ring is non-planar, with a puckering angle of 30.3°. The naphthyl ring, which is *cis* to the methyl substituent at C(3) in the four-membered ring, occupies a pseudo-equatorial position, to minimize cross-ring interaction with the methyl group.

Introduction. Structurally, phosphetanes are of twofold interest: firstly, comparison of phosphetane ring parameters with those of the carbocyclic analogues (cyclobutanes) provides valuable insight into the nature of ring strain in these compounds; and secondly, an empirical force field for phosphorus-containing compounds will need to be parameterized in such a way as to successfully describe these rather heavily strained heterocycles. The present investigation is concerned with a structural study of the highly substituted phosphetane (I).



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Experimental. Crystal ca 0.40 × 0.43 × 1.25 mm, Enraf–Nonius CAD-4 diffractometer, take-off angle 5°, graphite-crystal-monochromatized Cu K α radiation, 25 reflections ($28 < \theta < 33^\circ$) used to obtain cell dimensions by least-squares refinement, intensities of 1650 reflections ($0 \leq h \leq 9$, $0 \leq k \leq 14$, $0 \leq l \leq 19$) measured, ω - 2θ scan, $\theta_{\max} = 65^\circ$; three standard reflections monitored at intervals of 9000 s showed no variations in intensities; 1592 unique and 1575 observed reflections using $I \geq 3\sigma(I)$ criterion. Lorentz and polarization corrections applied; direct methods, *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) revealed positions of all non-H atoms. $R_{\text{int}} = 0.0074$ from merging equivalent reflections. F^2 magnitudes used in E map and full-matrix least-squares refinement of non-H atoms with anisotropic temperature factors, and H atoms (taken from a difference map) isotropically. All H-atom positions, except that for C(3)H which was refined freely, constrained to a bonding distance of 0.981 (8) Å from their relevant C atoms; final $R = 0.0345$, $wR = 0.0356$. Refinement of the structure of opposite chirality led to a final conventional R value of 0.0430; Hamilton's (1965) significance test confirms that our original (arbitrary) choice of enantiomer was correct. No absorption correction was applied but an empirical secondary extinction parameter refined to a final value of 2.034×10^{-2} . Weighting scheme for function $w = 0.9839/(\sigma^2|F_o| + 0.002724F_o^2)$ used to minimize $\sum w\Delta F^2$, $S = 1.04$. Max. peak height in final difference Fourier map = 0.239 e Å⁻³, ratio of max. LS shift to error 0.071. Form factors for non-H atoms from Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965). Calculations on an IBM 3033 computer at the University of Petroleum & Minerals using *SHELX76* (Sheldrick, 1976) programs.