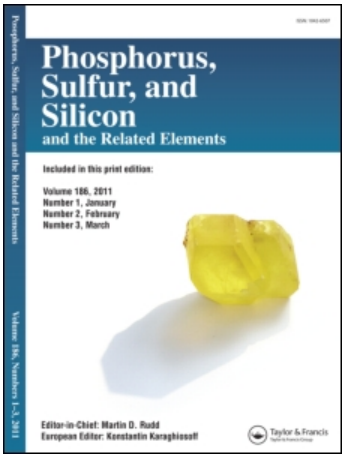

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TWO TRIAZOLE DERIVATIVES OF 2,2,3,4,4-PENTAMETHYLPHOSPHETAN 1-OXIDE WITH ANOMALOUS ^{1}H NMR CHEMICAL SHIFTS

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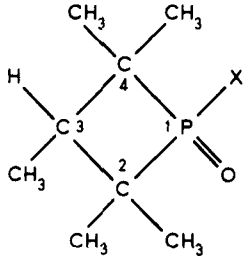
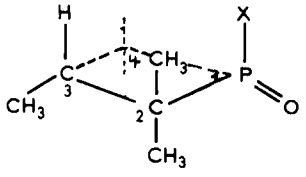
The benzotriazole and 3-amino-1,3,5-triazole derivatives of the title compound are reported, and display strong evidence that these aromatic rings orientate themselves in such a way as to deshield the substituents of the phosphetan ring.

2,2,3,4,4-Pentamethylphosphetan 1-oxides (I), $C_8H_{16}POX$, are easily prepared as the *trans* isomers (II) in which the phosphetan ring proton (C-3) is situated *trans*



(I)



side view

(II)

to the oxygen. The phosphetan ring is slightly bent (19°) along the C2–C4 axis as indicated in (II) as shown in the structure of tert-butyl compound $C_8H_{16}POBu^t$. *Cis* isomers can however be made and the naphthyl derivative $C_8H_{16}POC_{10}H_7$ is of this configuration.[2] In the acid, $C_8H_{16}PO_2H$, its anion, salts and complexes[3] this distinction is lost.

In an earlier paper[4] we described a series of alkyl- and arylthiophosphetans two of which, the phenyl and benzyl, showed unusual chemical shifts of the 2,4 *cis* methyl protons and the ring C-3 proton. We have now synthesised two new triazole compounds which show even more exaggerated effects on the ^{1}H n.m.r. resonances of these protons.

EXPERIMENTAL

1-Chloro-2,2,3,4,4-pentamethylphosphetan 1-oxide, $C_6H_{16}POCl$ (*trans*) was synthesised by the recommended method[5] and recrystallised from 60–80° petrolether before use. 3-Amino-1,2,4-triazole (Koch-light) and benzotriazole (B.D.H.) were used as supplied.

Preparation of 1-(1,2,4-triazole)-2,2,3,4,4-pentamethylphosphetan 1-oxide. $C_8H_{16}POCl$ (9.7 g, 0.05 mol), 3-amino-1,2,4-triazole (4.2 g, 0.05 mol) and triethylamine (5.1 g, 0.05 mol) reacted in refluxing toluene (800 ml) for 8 h under dry nitrogen. Two drops of Sterox ND, a surface activating agent, were added at the start of the reaction. The solution was subsequently filtered to remove Et_3NHCl and the solvent stripped on a rotary evaporator. The product (8.9 g) was a colourless oil which crystallized on standing and was recrystallized from 60–80° petrolether to yield 5.7 g (0.024 mol, 50%) of $C_8H_{16}PONC_2N_3H_2$ m.p. 164–5°C. Found: C, 49.08; H, 7.82; N, 23.32; P 12.74%; m/e 242. $C_{10}H_{19}N_4OP$ requires: C, 49.37; H, 7.85; N, 23.10; P 12.81%; RMM, 242.

The i.r. spectrum showed major absorbances at: 481 m, 517 m, 553 s, 645 m, 658 s, 668 m, 808 m, 1048 m, 1096 m, 1153 m, 1169 m, 1195 m, 1203 s, 1243 s, 1285 m, 1373 m, 1393 m, 1450 m, 1460 m, 1508 s, 1552 m, 1627 s, 1634 s, 2862 m, 2920 s, 2960 s, 2980 m, 2990 m, 3280 m, 3385 s, cm^{-1}.

The n.m.r. spectra in $CDCl_3$ showed resonances at: ^1H 0.97 (3-CH_3, dd; J_{HCCH}, 7.5 Hz; J_{PCCCH}, 1.5 Hz); 1.27 (2,4-CH_3; d; J_{PCCH}, 21 Hz); 1.39 (2,4-CH_3, d; J_{PCCH}, 19 Hz); 2.41 (3-H; dq; J_{HCCH}, 7.5 Hz; J_{PCCH}, 4.5 Hz) 6.49 (NH; m; br); 7.65 (CH; d; J_{HCNH}, 2 Hz): ^{13}C 6.9 (3-CH_3); 18.6 (2,4-CH_3); 22.5 (2,4-CH_3) 41.4 (C-3); 52.2 (C-2, C-4); 151.4 (CH triazole); 162.7 (CN_3): ^{31}P 64.56. [Referenced to $SiMe_4$ and H_3PO_4].

Preparation of 1-(1-benzotrizole)-2,2,3,4,4-pentamethylphosphetan 1-oxide. $C_8H_{16}POCl$ (9.7 g, 0.05 mol), benzotriazole (5.95, 0.05 mol) and triethylamine (5.1 g, 0.05 mol) reacted in refluxing toluene (200 ml) for 2 h under dry nitrogen. The solution was filtered to remove Et_3NHCl and the solvent stripped on a rotary evaporator to yield 13.6 g of pale yellow crystals of $C_8H_{16}PON_3C_6H_4$ which were recrystallized from 60–80° petrolether to give 10.9 g (0.04 mol, 80%), m.p. 135–6°C. Found: C, 60.58; H, 7.46; N, 15.57; P, 10.98%; m/e, 277. $C_{14}H_{20}N_3OP$ requires C, 60.64; H, 7.22; N, 15.16; P, 11.19%; RMM 277.

The i.r. spectrum showed major absorbances at: 430 m, 482 m, 513 vs, 557 s, 628 m, 662 m, 748 vs, 773 m, 910 m, 984 s, 1000 m, 1050 m, 1122 m, 1140 m, 1212 s, 1232 m, 1269 m, 1290 m, 1308 m, 1370 m, 1382 m, 1393 m, 1440 s, 1460 s, 1581 m, 1601 m, 2870 m, 2920 m, 2950 s, 2980 s cm^{-1}.

The n.m.r. spectra in $CDCl_3$ showed resonances at: ^1H 1.06 (3-CH_3; dd; J_{PCCCH3}, 2 Hz; J_{HCCH3}, 7.5 Hz); 1.22 (2,4-CH_3; d; J_{PCCH3}, 21 Hz); 1.52 (2,4-CH_3; d; J_{PCCH3}, 19.5 Hz); 2.63 (3-H; dq; J_{HCCH3}, 7.5 Hz; J_{PCCH}, 4.5 Hz); 7.82 (phenyl CH; m): ^{13}C 7.1 (3-CH_3); 18.8 (2.4-CH_3); 22.7 (2,4-CH_3); 41.7 (C-3); 52.8 (C-2, C-4); 114.0, 115.0, 119.7 (phenyl CH) 125, 129.1 (CN_3): ^{31}P 63.4. [Referenced to $SiMe_4$ and H_3PO_4].

trans-1-phenyl-2,2,3,4,4-pentamethylphosphetan 1-oxide was synthesized according to the method of Cremer and Chorvat[6] from dichlorophenylphosphine and 2,4,4-trimethylpent-2-ene in 46% yield.

RESULTS AND DISCUSSION

The protons attached to the carbons of the 2,2,3,4,4-pentamethylphosphetan ring have characteristic resonances in the ^1H n.m.r. spectrum.[4–9] They vary within

TABLE I
Protons affected by aromatic ring substituents on phosphorus, ^{1}H n.m.r. chemical shifts

Substituent[a]	*cis*-2,4-methyls	trans-2,4-methyls	C-3 H	Ref.
C_6H_5S—	1.27	1.33	1.89	4
$C_6H_5CH_2S$—	1.08	1.32	1.70	4
C_6H_5O—	1.27	1.29	1.80	7
$C_6H_5CH_2O$—	1.16	1.25	1.55	7
C_6H_5NH—	1.30	1.36	1.91	8
$C_6H_5CH_2NH$—	1.18	1.28	1.73	8
C_2H_3NH—	1.39	1.28	2.41	this work
$C_6H_4N_3$—	1.52	1.22	2.63	this work
C_6H_5—	1.12	1.41	2.04	this work and Reference 6

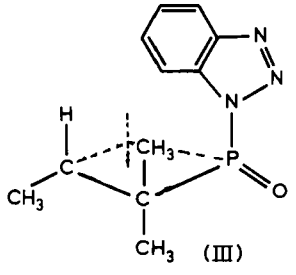
[a] All *trans* derivatives.

very narrow limits and those of the C-3 methyl vary least of all, being always observed as a pair of doublets centred on 0.86–0.97 in the large number of compounds reported. The same is true for the C-2 and C-4 methyls which occur as a pair of doublets in the range 1.16–1.43, the pair being generally separated by *ca* 0.3 ppm. Finally the solitary C-3 ring proton is to be found at 1.66–1.86.

The above general observations also are true for many $C_8H_{16}POX$ compounds when the X group contain an aromatic ring except in the notable cases of X = C_6H_5S and $C_6H_5CH_2S$ when there is a marked change in C-3 H in the former and in the chemical shifts of one C-2, C-4 CH_3 doublet in the latter, see Table. This also lists the δ_H values of these protons in other phenyl containing substituents and a similar effect on C-3 H can be seen for $C_8H_{16}PONHC_6H_5$ and on the cis C-2, C-4 CH_3 of $C_8H_{16}PONHCH_2C_6H_5$.

These effects can be explained by structures in which the phenyl rings are orientated in such a manner that the induced magnetic field is deshielding the C-3 H region which it might do if the plane of the benzene ring were in the vertical plane of the molecule. In this arrangement it could also shield or deshield the *cis* methyl protons depending upon its orientation. Shielding might be possible with the extra flexibility of a CH_2 group as the Table shows.

Long-range changes are even more apparent in the two triazole compounds reported here. Table I shows a remarkable downfield shift in the C-3 H signals to 2.41 and 2.63 ppm. And whereas the *cis* methyl signals are not affected by the amino-triazole derivative they are by the benzotriazole derivative and are also deshielded. This is quite at variance with the expected trend and suggests that in this molecule the aromatic ring can orientate itself in space so as to deshield both regions of space, which it could do given that the benzoltriazole rings were in the vertical plane and held there by restricted rotation about the P–N bond (III).



(III)

All the benzene rings in the above compounds, and the triazole ring of the amino-1,2,4-triazole are separated from the phosphorus atom by an intervening atom. This gives the aromatic ring the option of placing itself well away from the C-3 H and the phosphetan ring if it so wished.

Even in the *trans* phenyl derivative, $C_8H_{16}POPh$, the effect on the C-3 H is still recognizable as is the shielding of the *cis* methyls. From these observations it seems reasonable to conclude that in solution aromatic substituents on phosphorus adopt a configuration perpendicular to the phosphetan ring. In some cases this might be due to π delocalization involving phosphorus but in others this cannot be the case.

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