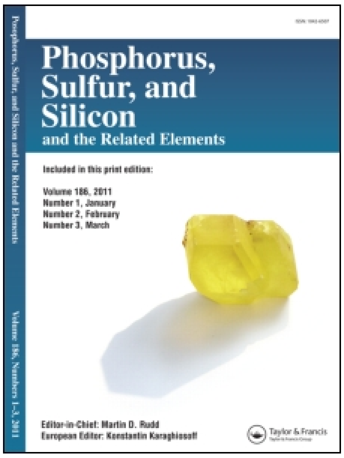

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Synthesis and Characterisation of Two Examples of Unsymmetrically Disubstituted Cyclotetrathiazenes, 1,5-(X)(Y)S_4N_4[X = Ph_3PN- and Y = i) (p-$CH_3C_6H_4$) Ph_2PN- and ii) (P-$CH_3C_6H_4$)$_2$PhPN-]

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SYNTHESIS AND CHARACTERISATION OF TWO EXAMPLES OF UNSYMMETRICALLY DISUBSTITUTED CYCLOTETRATHIAZENES, 1,5-(X)(Y)S_4N_4[X = Ph_3PN- and Y = i) (p-$CH_3C_6H_4$)Ph_2PN- and ii) (p-$CH_3C_6H_4)_2PhPN$-]

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Abstract 1,5- [(p-tolyl)diphenylphosphinimino] (triphenylphosphinimino)tetrasulphurtetranitride,(I) and 1,5-[di(p-tolyl)phenylphosphinimino] (triphenylphosphinimino)tetrasulphurtetranitride,(II) are the first examples of heterodisubstituted tetrasulphurtetranitride derivatives to be made. Their synthesis and structural characterization are described.

INTRODUCTION:

1,5-Disubstituted S_4N_4 derivatives are one of the interesting classes of ring systems among inorganic heterocycles as they offer scope to realize different stereoisomer possibility (Fig. 1).

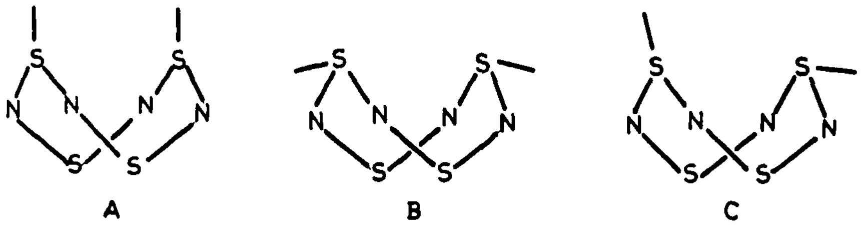

FIGURE 1 Possible structural modifications of 1,5 disubstituted S_4N_4 derivatives.

Of the nine compounds of this type known so far, X-ray structure determination in case of $X_2S_4N_4$ (X = Cl^1, Me_2N-^{2} and Ph_3PN-^{3}) has established an exo-endo-orientation of groups in them. Variable temperature ^1H-nmr study has established exo-endo structure for X = NC_4H_8 while the compound $(C_5H_{10}N)_2S_4N_4$ is shown to exist with structure (B) and (C) at different temperatures in solution[4]. On the basis of low temperature ^{31}P-nmr study, an exo-endo- structure for $[(OC_4H_8N)Ph_2PN]_2S_4N_4$ was suggested recently[5]. Interestingly, the observation of a singlet in the ^{19}F-nmr spectra of $X_2S_4N_4$ (X = F[6] and $(CF_3)_2NO$-[7]) was used as the criteria to propose an exo-exo-(B in fig.1) orientation of groups in them. The structural dichotomy exhibited by these compounds has been analysed in the light of MNDO calculations by Oakley in 1984[8]. Recently, Thomas and Rao have also shown the facile ring contraction in solution of 1,5-$[(OC_4H_8N)Ph_2PN]_2S_4N_4$ to the corresponding -S_3N_3 heterocycle[5].

1,5-disubstituted S_4N_4 derivatives possessing different substituents at the 1 and 5 positions provide additional interest as with such examples, positional isomerism possibility also exists. Examples of such compounds are not known so far. Our recent study on the reactions of S_4N_4 with two different phosphines taken at a time has shown the prospect of yielding such compounds for the first time[9]. We report here the details of the preparation of two such examples and their structural characterization.

EXPERIMENTAL:

S_4N_4[10] and $(p\text{-tolyl})_2PhP$[11] were synthesized using reported procedures. Ph_3P(Fluka) and $(p\text{-tolyl})Ph_2P$(Aldrich) were commerical samples used as such. All reactions were performed under an atmosphere of dry argon/nitrogen. Dry and distilled solvents were used.

Synthesis of 1,5-$[(p\text{-}CH_3C_6H_4)(C_6H_5)_2PN][(C_6H_5)_3PN]S_4N_4$(I)

To a stirred solution of Ph_3P (0.36 g, 1.35 mmol) and (p-tolyl)-Ph_2P(0.76 g, 2.70 mmol) in CH_3CN at 25°C, S_4N_4(0.25 g, 1.35 mmol) was added as solid, all at a time. Reaction began slowly with the formation of an yellow precipitate and red filtrate. After 24 hours the reaction mixture was filtered. The yellow precipitate was found to be a pure sample of $[(p\text{-tolyl})Ph_2PN]_2(Ph_3PN)S^+S_4N_5^-$ (0.21 g, 28%). The filtrate was concentrated to two thirds of the original volume and cooled at 0°C for one day to isolate a pale yellow microcrystalline substance, characterized as 1,5-$[(p\text{-tolyl})Ph_2PN]$-$(Ph_3PN)S_4N_4$ (I) (0.08 g, 12%), m.p.: 120°C (dec) I.R.: (KBr disc, 1800-400 cm^{-1}): 1604 (vw), 1590(w), 1505(vw), 1484(m), 1440(s), 1400(vw), 1340(vw), 1313(vw), 1190(sh,w), 1160(sh,m), 1134(sh,s), 1118(vs),1087(s), 1028(vw), 1020(vw), 1000(w), 968(s), 910(vs), 854(w), 815(w), 807(w), 779(w), 760(m), 745(m), 722(s), 704(m), 692(s), 632(s), 605(w), 588(vw), 548(m), 525(s), 494(m), 464(m), 420(vw); ^{1}H-nmr [-40°C,$CDCl_3$]: δ(in ppm): 2.02 and 2.30 (2s, 3H), 7.05-7.60(m,28H) {^{1}H} ^{31}P-nmr: [$CDCl_3$,-60°C]: δ(in ppm): 25.25(m) and 18.82(s); Anal.Calcd. for $C_{37}H_{32}N_6P_2S_4$: C,59.16; H, 4.30; N, 11.20; Found: C, 59.19, H, 4.33; N, 11.18.

Filtrate on further concentration and cooling also yielded $(p\text{-tolyl})Ph_2PN\text{-}S_3N_3$(0.05 g, 8%) and the sulphides of both phosphines.

Synthesis of 1,5-$[(p\text{-}CH_3C_6H_4)_2(C_6H_5)PN][(C_6H_5)_3PN]S_4N_4$ (II)

Tetrasulphurtetranitride (0.19 g, 1.03 mmol) was reacted with Ph_3P (0.27 g, 1.03 mmol) and $(p\text{-tolyl})_2PhP$ (0.60 g, 2.06 mmol) in CH_3CN (20 ml) as in the above reaction. Filtration of the reaction mixture after 24 hrs. gave an yellow solid (0.20 g) found to be a mixture of $[(p\text{-tolyl})_2PhPN]_2[Ph_3PN]S^+S_4N_5^-$ and 1,5-$[(p\text{-tolyl})_2$-$PhPN](Ph_3PN)S_4N_4$,(II). This was extracted with cold benzene (5 x 5 ml) and to the pale yellow benzene extract was added CH_3CN (10 ml) and cooled in the refrigerator for two days to isolate a light yellow microcrystalline solid characterized as 1,5- $[(p\text{-tolyl})_2$-$PhPN](Ph_3PN)S_4N_4$, (0.12 g, 23%). m.p.: 92°C (dec), IR (Nujol mull, 1600-600 cm^{-1}): 1597(w), 1586(vw), 1500(vw), 1476(m), 1438(s), 1397(vw), 1340(sh,vw), 1310(vw), 1190(vw), 1160(m), 1132(s), 1112(vs), 1080(s), 1026(vw), 1017(vw), 998(w), 964(vs), 910(vs), 850(w), 808(m), 775(w), 759(m), 745(sh.w), 720(s), 691(s), 659(m), 635(s), 615(s); ^{1}H-nmr [$CDCl_3$ -40°C]: δ(in ppm): 2.05 and 2.28 (2s,6H), 6.80-7.60

(m,28H); $\{^1H\}^{31}P$-nmr [$CDCl_3$ -60°C, external H_3PO_4] δ (in ppm) 18.66(s), 25.25(m). Anal. Calcd. for: $C_{38}H_{34}N_6P_2S_4$; C, 59.64; H, 4.48; N, 10.99; Found: C, 59.78, H, 4.53; N, 11.06.

From the filtrate, (p-tolyl)$_2$PhPN-S_3N_3 (0.06 g, 13%) as well as a mixture of (p-tolyl)$_2$PhPS and Ph_3PS were isolated.

RESULTS AND DISCUSSION:

Pale yellow crystalline compounds (I) and (II) are isolated in Ca. 25% yield from a 1:1:2 reaction of S_4N_4, Ph_3P and the other phosphine, (p-tolyl)Ph_2P or (p-tolyl)$_2$PhP. The yields are no better and their isolation is not easier from the other stiochiometric reactions tried (1:1:1, 1:2:1 and 1:2:2). Acetonitrile is the solvent of preference for their formation. Unlike 1,5-$(Ph_3PN)_2S_4N_4$, compounds I and II are isolated from the filtrate of the reaction. Reactions are in general quite complex and other cyclic derivatives are also isolated (see experimental). Similar to 1,5$(Ph_3PN)_2S_4N_4$ and the recent 1,5-$[(OC_4H_8N)Ph_2PN]_2S_4N_4$, compounds (I) and (II) melt to a red liquid with decomposition on heating.

The infrared spectra of (I) and (II) are remarkably similar to their homo-disubstituted analogues and to the reported 1,5-$(Ph_3PN)_2S_4N_4$. Observation of two distinct peaks around 810 cm^{-1} for p-tolyl group in (I) and a broad peak around the same value for di(p-tolyl) group in (II) gave a clue to positional isomer possibility. Low temperature proton nmr spectra of (I) and (II) showed the corresponding signals in their expected intensities. Their spectra at -40°C clearly show two methyl signals although they contain only one (p-tolyl)Ph_2PN- or (p-tolyl)$_2$PhPN- group which suggest the possible existence of positional isomers in solution. Additional interesting features were observed in their low temperature ^{31}P-nmr spectra (Fig.2). The complexity of the signals due to the phosphinimino group in the exo- position cannot be explained fully by the presence of positional isomers alone.

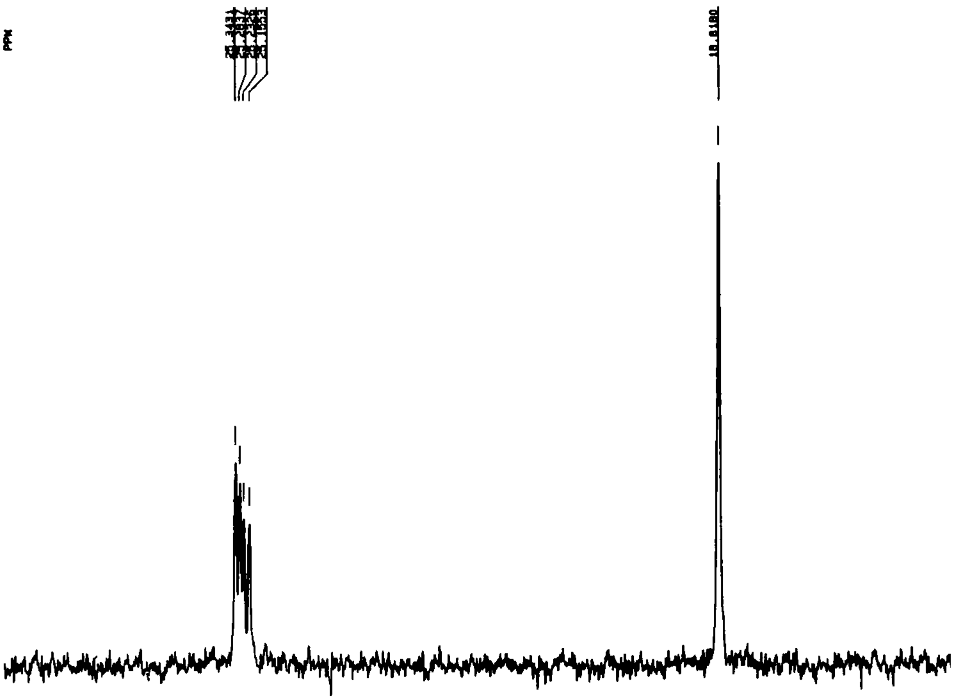

FIGURE 2 $\{^1H\}$ ^{31}P-nmr spectrum (121.5 MHz) of 1,5-[(p-tolyl)Ph_2PN][Ph_3PN]S_4N_4 at -60°C.

We therefore propose the existence of stereo isomers as well, in solution. That is, those with slightly differing orientations of the exo- group while the endo-group is more or less frozen at that temperature. This is further supported by the fact that the phosphorus shifts of the signals at the exo- position are only marginally different from one another. Similar nmr features (^1H- and ^{31}P-) were noticed for compound (II) as well. These first time observations appear to be incongruous to the conclusion drawn by Oakley on the basis of theoretical calculations. However it may be mentioned that the homo-disubstituted derivatives 1,5-$(Ph_3PN)_2S_4N_4$,[12] 1,5-[(p-tolyl)Ph_2PN]$_2S_4N_4$ and 1,5-[(p-tolyl)$_2PhPN$]$_2$-S_4N_4[12] show only the expected two equally intense phosphorus signals in their ^{31}P-nmr spectra.

The changes occuring in the spectra (both ^{1}H- and ^{31}P-) with the rise in temperature as well as the growing intensity of the absorptions at 480 and 330 nm in the UV-Visible spectra of (I) and (II) in CH_2Cl_2 at room temperature are in conformity with the recently reported ring contraction[5]. However, in these cases, $R-S_3N_3$ where R is Ph_3PN- and (p-tolyl)Ph_2PN- or (p-tolyl)$_2PhPN$- are isolated.

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