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# Formation and X-ray Crystal Structures of $(Ph_2PN)_2(NS(O)NPPh_2NPPh_2NH_2)$ and $Et_2NH_2^+[(Ph_2PN)_2(NSO_2)]^-$ from the Aerial Hydrolysis of $(Ph_2PN)_2(NSNR_2)$ (R = Me, Et)

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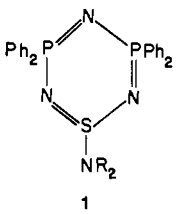
When solutions of $(Ph_2PN)_2(NSNR_2)$ (**1**) in acetonitrile are allowed to stand at room temperature in air, two white crystalline products, **4** and **5**, are formed, in addition to the previously characterized twelve-membered ring dimer, $(Ph_2PN)_4(NSNR_2)_2$ (**2**). The $^{31}P$ NMR spectrum of **4** exhibits a singlet at +20.7 ppm, while the spectrum of **5** shows three signals at +18.7, +17.1, and 0.0 ppm in the approximate intensity ratio 2:1:1. The crystal and molecular structures of **4** and **5** have been determined by X-ray diffraction. Crystals of **4** are triclinic, space group $P\bar{1}$, with $a = 11.0853$ (13) Å, $b = 12.4189$ (9) Å, $c = 10.6956$ (12) Å, $\alpha = 96.008$ (7)°, $\beta = 103.590$ (10)°, $\gamma = 96.517$ (8)°, and $Z = 2$. The refined structure ($R = 0.043$) shows **4** to be a salt containing the six-membered anionic ring $(Ph_2PN)_2(NSO_2)^-$. Each ion is found to have hydrogen-bonding interactions with two crystallographically independent ions of opposite charge. Thus, each $Et_2NH_2^+$ cation has both a N-H---O and a N-H---N interaction. The NSNPN unit of the anionic ring is planar to within 0.05 Å while the remaining phosphorus atom lies 0.45 Å out of this plane. Internal dimensions of the anion show a distortion of the ring, presumably as a result of the hydrogen bonding. Crystals of **5** are monoclinic, space group $P2_1/c$, with $a = 17.287$ (4) Å, $b = 15.224$ (2) Å, $c = 18.320$ (4) Å, $\beta = 114.906$ (9)°, and $Z = 4$. The refined structure ($R = 0.036$) shows **5** to be a mixed phosphazene–sulfanuric ring of the type $(Ph_2PN)_2(NS(O)R)$ where R is the diphosphazenyl chain, $NPPh_2NPPh_2NH_2$. The $(Ph_2PN)_2(NS)$ ring adopts a chair conformation, with sulfur and one nitrogen atom lying on opposite sides of the least-squares plane. The conformation of the $-NPPh_2NPPh_2NH_2$ chain is such that an intramolecular N-H---O hydrogen-bonding interaction is formed.

## Introduction

We have recently reported that six-membered rings of the type $(Ph_2PN)_2(NSNR_2)$ (**1**) (R = Me, Et, $(-CH_2-)_5$) undergo



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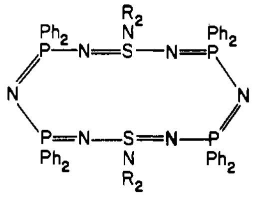

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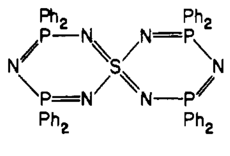

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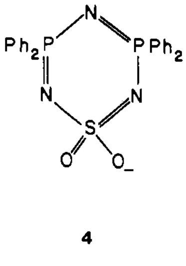
a ring-opening dimerization to a twelve-membered ring, **2**, either in acetonitrile at room temperature or in the solid phase above ca. 150 °C.[1] The latter compounds, **2**, are intermediates in the thermal conversion of **1** to the spirocyclic compound **3**.[2]

We now describe the formation, spectroscopic characterization, and X-ray structural determination of two other products, **4** and **5**, formed when solutions of **1** are allowed to stand at room temperature in the presence of air and/or moisture.



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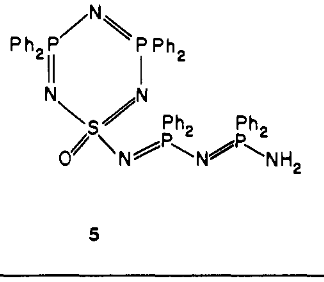

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## Experimental Section

**Reagents and General Procedures** $(Ph_2PN)_2(NSCl)$[3] and $(Ph_2PN)_2(NSNMe_2)$[1] were prepared by the literature procedures. Diethylamine, methylene dichloride ($P_2O_5$), and acetonitrile were freshly distilled before use.

Infrared spectra were recorded as Nujol mulls (CsI windows) on a Perkin-Elmer 467 grating spectrophotometer, and $\{^1H\}^{31}P$ NMR spectra were obtained by using a Varian XL-200 instrument. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ.

**Formation of $Me_2NH_2^+[(Ph_2PN)_2(NSO_2)]^-$ and $(Ph_2PN)_2(NS(O)NPPh_2NPPh_2NH_2)$ from the Aerial Hydrolysis of $(Ph_2PN)_2(NSNMe_2)$.** A solution of $(Ph_2PN)_2(NSNMe_2)$ (0.78 g) in a mixture of acetonitrile (25 mL) and methylene dichloride (5 mL) was allowed to stand in a loosely stoppered flask at 23 °C for 5 days. Colorless crystals of the dimer $(Ph_2PN)_4(NSNMe_2)_2$ (0.20 g) were deposited and removed by filtration.[1] After several days a second crop of white crystals appeared, which were identified as $Me_2NH_2^+[(Ph_2PN)_2(NSO_2)]^-$ (0.10 g). Anal. Calcd for $C_{26}H_{28}N_4O_2P_2S$: C, 59.75; H, 5.41; N, 10.72; S, 6.14. Found: C, 59.73; H, 5.58; N, 10.61; S, 6.25. $\{^1H\}^{31}P$ NMR (in $CDCl_3$): +20.7 ppm (s, 85% $H_3PO_4$ as external reference). IR (Nujol): 3063 (w), 3040 (w), 1479 (m), 1440 (s), 1242 (s), 1185 (s), 1170 (s), 1164 (s), 1152 (vs), 1124 (vs), 1114 (vs), 1080 (s), 1068 (s), 1027 (m), 989 (m), 840 (m), 828(m), 752 (s), 724 (s), 700 (s), 574 (m), 539 (s), 525 (s) $cm^{-1}$.

The filtrate was allowed to stand for another few days whereupon white crystals of $(Ph_2PN)_2(NS(O)NPPh_2NPPh_2NH_2)$ (0.15 g) were obtained. Anal. Calcd for $C_{48}H_{42}N_6OP_4S$: C, 65.89; H, 4.85; N, 9.61; S, 3.66. Found: C, 65.76; H, 4.93; N, 9.67; S, 4.09. $\{^1H\}^{31}P$ NMR: +18.7 (s), +17.1 (s), 0.0 ppm (s) in the approximate intensity ratio 2:1:1. IR (Nujol): 3370 (w), 3240 (w), 3050 (w), 1473 (m), 1437(s), 1309 (m), 1299 (m), 1273 (m), 1198 (s), 1188 (s), 1162 (vs), 1154 (vs), 1127 (s), 1116 (s), 1096 (vs), 1071 (m), 1028 (m), 734 (s), 720 (s), 701 (s), 570 (m), 549 (s), 531 (m), 521 (m), 510 (m) $cm^{-1}$.

**Aerial Hydrolysis of $(Ph_2PN)_2(NSNEt_2)$.** Diethylamine (ca. 0.5 mL) in methylene dichloride (5 mL) was added dropwise (20 min)

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(1) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 702.

(2) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 700.

(3) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1982**, 982.

(4) Computing was performed at the University of Calgary with use of the X-RAY 76 package of crystallographic programs: Stewart, J. M., Ed. Technical Report TR-446; Computer Science Center, University of Maryland: College Park, MD.

(5) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

(6) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 149.

0020-1669/84/1323-1531$01.50/0

**Table I.** Crystal Data

| | $Et_2NH_2^+[(Ph_2PN)_2(NSO_2)]^-$ (4) | $(Ph_2PN)_2(NS(O)NPPh_2NPPh_2NH_2)$ (5) |
|---|---|---|
| formula | $C_{28}H_{32}N_4O_2P_2S$ | $C_{48}H_{42}N_6OP_4S$ |
| fw | 550.60 | 874.87 |
| crystal descrip | colorless blocks | colorless plates |
| space group | $P\bar{1}$ | $P2_1/c$ |
| $a$, Å | 11.0853 (13) | 17.287 (4) |
| $b$, Å | 12.4189 (9) | 15.224 (2) |
| $c$, Å | 10.6956 (12) | 18.320 (4) |
| $\alpha$, deg | 96.008 (7) | 90 |
| $\beta$, deg | 103.590 (10) | 114.906 (9) |
| $\gamma$, deg | 96.517 (8) | 90 |
| $V$, Å$^3$ | 1405.0 (5) | 4373 (1) |
| $Z$ | 2 | 4 |
| $D_{calcd}$, g cm$^{-3}$ | 1.30 | 1.33 |
| radiation | Mo K$\alpha$; $\lambda = 0.71069$ Å (graphite monochromator) | |
| temp, °C | 23 (1) | 23 (1) |
| max $\theta$, deg | 25 | 24 |
| scan range ($\Delta\omega$), deg | $1.5(0.6 + 0.347 \tan \theta)$ | $1.5(0.6 + 0.347 \tan \theta)$ |
| octants collcd | $\pm h, \pm k, -l$ | $+h, +k, \pm l$ |
| cryst dimens, mm | 0.33 × 0.31 × 0.27 | 0.45 × 0.40 × 0.19 |
| boundary planes | 12; $\{100\}$, $\{010\}$, $\{001\}$, $\{110\}$, $\{1\bar{1}0\}$, $\{01\bar{1}\}$ | 8; $\{100\}$, $\{001\}$, $(011)$, $(0\bar{1}\bar{1})$, $(11\bar{1})$, $(\bar{1}\bar{1}1)$ |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 2.63 | 2.68 |
| no. of unique data | 4938 | 6837 |
| no. of obsd data ($I > 3\sigma(I)$) | 2482 | 2625 |
| $R$, $R_w$ | 0.043, 0.026 | 0.036, 0.026 |
| GOF | 1.29 | 1.34 |

to a stirred solution of $(Ph_2PN)_2(NSCl)$ (1.12 g) in methylene dichloride (25 mL). After 3 h at 23 °C solvent was removed to give a reddish semisolid residue that was treated with acetonitrile (30 mL). The white precipitate was separated by filtration and washed with water (to remove $Et_2NH_2^+Cl^-$). The insoluble white product was identified as the dimer $(Ph_2PN)_4(NSNEt_2)_2$,[1,7] which also deposited as white crystals from the acetonitrile solution (total yield 0.70 g). The MeCN filtrate deposited pale yellow crystals of $Et_2NH_2^+[(Ph_2PN)_2(NSO_2)]^-$ on standing at 23 °C for 2 weeks. Anal. Calcd for $C_{23}H_{32}N_4O_2P_2S$: C, 61.07; H, 5.87. Found: C, 61.15; H, 5.87. $\{^1H\}^{31}P$ NMR: +20.6 ppm (s). IR (Nujol): 3080 (vw), 3059 (vw), 3041 (vw), 3035 (vw), 1435 (s), 1215 (m), 1185 (m), 1150 (vs), 1135 (vs), 1120 (s), 1103 (s), 1080 (s), 1065 (m), 1048 (m), 1025 (m), 821 (m), 725 (m), 700 (s), 571 (m), 545 (m), 527 (s) cm$^{-1}$.

## X-ray Analysis

The crystal data and experimental conditions are given in Table I. Cell constants and orientation matrices were determined by least-squares refinement of the diffraction geometry for 25 accurately centered reflections having $15 < \theta < 19°$ for **4** and $12 < \theta < 17°$ for **5**. The space groups were determined by using the indexing routines of the diffractometer and by examination of the intensities measured during data collection. In the case of **4**, $P\bar{1}$ was the final choice based on the centric distribution of $E$ values.

The data were collected on an Enraf-Nonius CAD4F automated diffractometer using an $\omega$–$2\theta$ scan of 96 steps, of which the central 64 steps were taken as the peak, $P$, and the first and last 16 steps were taken as backgrounds, $B1$ and $B2$. The intensity was calculated as $I = [P - 2(B_1 + B_2)]Q$, where $Q$ is the scan rate, and the standard deviation of the intensity as $\sigma(I) = [P + 4(B_1 + B_2)]^{1/2}Q$. The data were corrected for Lorentz and polarization effects, and $E$ values were calculated with use of a K curve.[4] Absorption corrections were not applied.

Atomic scattering factors were those of Cromer and Mann.[5] Real and anomalous dispersion corrections were applied to all non-hydrogen atoms.[6] With each structure, initial coordinates for P, S, and most N atoms were obtained by using direct methods (MULTAN 78). Structure factor and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. Refinement was carried out by full-matrix least-squares techniques based on $F$, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where the weight $w$ was defined as $[\sigma^2(F_o)]^{-1}$ for both structures. All H atoms were readily located from difference Fourier maps, and C–H atoms were included in idealized positions ($sp^2$ or $sp^3$ hybridization at C; C–H = 0.95 and 1.00 Å, respectively) but not refined. Thermal parameters were set to 1.1 × $U_{equiv}$ of the C to which they are bonded.

For the final cycles, positional and anisotropic thermal parameters for the non-hydrogen atoms, positional and isotropic thermal parameters for N–H atoms, and an isotropic extinction correction were refined, and C–H positional parameters were recalculated. The model for **4** converged for 3691 reflections (observed reflections plus those for which $I_c > 3\sigma(I_o)$) and 343 variables with the agreement factors $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.043$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.026$. In the final cycle, the maximum shift/error was 0.6, the goodness of fit value was 1.29, and the isotropic extinction parameter was 0.80 (3) × $10^{-4}$. The highest peak in a difference Fourier map is 0.55 e Å$^{-3}$ and is associated with O(1). The model for **5** converged for 4738 reflections (observed reflections plus those for which $I_c > 3\sigma(I_o)$) and 549 variables with the agreement factors $R = 0.036$ and $R_w = 0.026$. The maximum shift/error was 0.5, and the goodness of fit value was 1.34. An isotropic extinction parameter could not be refined successfully. A difference Fourier map showed the peak of highest electron density (0.45 e Å$^{-3}$) to be associated with C(82).

## Results and Discussion

**Aerial Hydrolysis of $(Ph_2PN)_2(NSNR_2)$.** When solutions of **1** (R = Me, Et, $(-CH_2-)_5$) in acetonitrile are allowed to stand at room temperature, the first product to crystallize out is the dimer, **2**.[1,7] Two other white crystalline products, **4** and **5**, are deposited from the acetonitrile filtrate when precautions to exclude air or moisture from the solution are not taken. The $^{31}P$ NMR spectra indicated that these products had quite different structures. Thus, **4** gave rise to a singlet at +20.7 ppm while the $^{31}P$ NMR spectrum of **5** consisted of three singlets at +18.7, +17.1, and 0.0 ppm with approximate intensities 2:1:1. The infrared spectra of both products showed bands attributable to N–H stretching vibrations at ca. 3050 cm$^{-1}$ (**4**) and 3370, 3240, and 3050 cm$^{-1}$ (**5**) as well as strong bands at ca. 1440 cm$^{-1}$ suggestive of >S=O or $SO_2$ groups, indicating that they result from hydrolysis and/or oxidation. In order to establish the molecular structures of **4** and **5**, we carried out the X-ray structural determinations described below.

**Crystal and Molecular Structure of 4.** The final atomic coordinates of the non-hydrogen atoms of the ions are given in Table II. Thermal parameters, parameters for the hydrogen atoms, the bond lengths and angles associated with phenyl rings, and the lists of structure factor amplitudes are available as supplementary material. Selected bond lengths and angles

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(7) Chivers, T.; Rao, M. N. S., unpublished results.

**Table II.** Positional Parameters (×$10^4$) for the Refined Atoms of $Et_2NH_2^+[(Ph_2PN)_2(NSO_2)]^-$

| atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| S | 6668.7 (8) | 2085.9 (7) | 363.0 (9) |
| P(1) | 7269.1 (8) | 2389.2 (7) | 2862.1 (9) |
| P(2) | 9097.9 (9) | 2406.7 (8) | 1980.4 (9) |
| N(1) | 6249 (2) | 2546 (2) | 1649 (2) |
| N(2) | 8638 (2) | 2945 (2) | 3197 (2) |
| N(3) | 8093 (3) | 2088 (3) | 625 (3) |
| O(1) | 6068 (3) | 982 (2) | 24 (3) |
| O(2) | 6318 (3) | 2720 (3) | −620 (3) |
| N(4) | 5520 (3) | −753 (2) | −1899 (3) |
| C(1) | 5092 (5) | −273 (3) | −3095 (4) |
| C(2) | 3881 (4) | 161 (4) | −3138 (5) |
| C(3) | 6733 (4) | −1189 (3) | −1774 (5) |
| C(4) | 7021 (4) | 1750 (4) | −599 (5) |
| C(11) | 6611 (3) | 3170 (2) | 4232 (3) |
| C(12) | 5443 (3) | 3450 (3) | 4218 (3) |
| C(13) | 4905 (3) | 3303 (3) | 5254 (4) |
| C(14) | 5551 (4) | 2890 (3) | 6302 (4) |
| C(15) | 6720 (4) | 2628 (3) | 6333 (4) |
| C(16) | 7260 (3) | 2771 (3) | 5300 (4) |
| C(21) | 7372 (3) | 4713 (3) | 2678 (3) |
| C(22) | 6402 (3) | 5110 (3) | 1879 (4) |
| C(23) | 6492 (4) | 6217 (4) | 1759 (4) |
| C(24) | 7538 (5) | 6917 (3) | 2434 (5) |
| C(25) | 8509 (5) | 6544 (4) | 3223 (5) |
| C(26) | 8431 (4) | 5447 (3) | 3352 (4) |
| C(31) | 9768 (3) | 1209 (3) | 2430 (4) |
| C(32) | 9647 (4) | 312 (4) | 1568 (5) |
| C(33) | 10171 (7) | −602 (5) | 1921 (8) |
| C(34) | 10801 (7) | −619 (6) | 3089 (9) |
| C(35) | 10948 (7) | 261 (6) | 3983 (7) |
| C(36) | 10438 (6) | 1192 (4) | 3651 (5) |
| C(41) | 10366 (3) | 3315 (3) | 1723 (4) |
| C(42) | 10368 (4) | 3574 (3) | 511 (4) |
| C(43) | 11346 (6) | 4312 (4) | 345 (5) |
| C(44) | 12299 (5) | 4773 (4) | 1384 (6) |
| C(45) | 12314 (4) | 4524 (4) | 2605 (5) |
| C(46) | 11348 (4) | 3790 (3) | 2768 (4) |
| H1N[a] | 4798 (30) | −1421 (20) | −1824 (30) |
| H2N[a] | 5646 (30) | −223 (20) | −1076 (30) |

[a] H1N and H2N are bonded to N(4) and were refined in the final cycles.

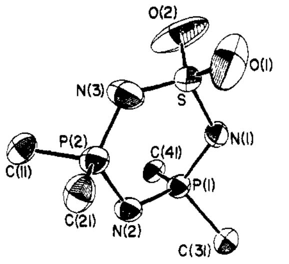

**Figure 1.** ORTEP drawing (50% probability ellipsoids) of the anion of $Et_2NH_2^+[(Ph_2PN)_2(NSO_2)]^-$ showing the atom-numbering scheme. For clarity only the α-C atoms of the phenyl rings are shown.

**Table III.** Positional Parameters (×$10^4$) for the Refined Atoms of $(Ph_2PN)_2(NS(O)NPPh_2NPPh_2NH_2)$

| atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| S | 7112.8 (7) | −920.9 (8) | 399.2 (7) |
| P(1) | 8131.4 (8) | −2345.6 (8) | 1164.8 (7) |
| P(2) | 7483.3 (7) | −1332.0 (8) | 2006.5 (7) |
| P(3) | 7570.2 (7) | 739.4 (8) | −14.9 (7) |
| P(4) | 6091.9 (8) | 1511.6 (8) | 180.1 (7) |
| N(1) | 7527 (2) | −1834 (2) | 360 (2) |
| N(2) | 7930 (2) | −2227 (2) | 1936 (2) |
| N(3) | 6925 (2) | −838 (2) | 1169 (2) |
| N(4) | 7775 (2) | −185 (2) | 432 (2) |
| N(5) | 6949 (2) | 1443 (2) | 91 (2) |
| N(6) | 5359 (2) | 799 (2) | −318 (2) |
| O | 6303 (2) | −830 (2) | −308 (1) |
| C(11) | 8051 (3) | −3488 (3) | 906 (3) |
| C(12) | 7650 (3) | −3767 (3) | 132 (3) |
| C(13) | 7605 (4) | −4654 (4) | −50 (4) |
| C(14) | 7984 (4) | −5250 (4) | 549 (4) |
| C(15) | 8384 (4) | −4984 (4) | 1318 (4) |
| C(16) | 8415 (3) | −4094 (3) | 1496 (3) |
| C(21) | 9231 (3) | −2081 (3) | 1434 (2) |
| C(22) | 9828 (3) | −2202 (3) | 2208 (3) |
| C(23) | 10675 (3) | −2022 (3) | 2428 (3) |
| C(24) | 10941 (3) | −1712 (4) | 1876 (3) |
| C(25) | 10360 (3) | −1577 (4) | 1114 (3) |
| C(26) | 9508 (3) | −1770 (3) | 889 (2) |
| C(31) | 6778 (3) | −1554 (3) | 2477 (2) |
| C(32) | 6178 (3) | −933 (3) | 2428 (3) |
| C(33) | 5644 (3) | −1067 (3) | 2809 (3) |
| C(34) | 5723 (3) | −1827 (4) | 3237 (3) |
| C(35) | 6299 (3) | −2440 (3) | 3278 (3) |
| C(36) | 6831 (3) | −2317 (3) | 2893 (3) |
| C(41) | 8285 (2) | −606 (3) | 2701 (3) |
| C(42) | 8742 (3) | −63 (3) | 2422 (2) |
| C(43) | 9367 (3) | 489 (3) | 2948 (3) |
| C(44) | 9546 (3) | 512 (4) | 3748 (3) |
| C(45) | 9097 (3) | −20 (4) | 4025 (3) |
| C(46) | 8477 (3) | −584 (3) | 3511 (3) |
| C(51) | 8608 (3) | 1258 (3) | 371 (2) |
| C(52) | 9345 (3) | 771 (3) | 734 (3) |
| C(53) | 10140 (3) | 1182 (4) | 1015 (3) |
| C(54) | 10182 (4) | 2076 (5) | 932 (4) |
| C(55) | 9463 (4) | 2564 (4) | 585 (4) |
| C(56) | 8676 (3) | 2161 (3) | 298 (3) |
| C(61) | 7274 (3) | 594 (3) | −1078 (2) |
| C(62) | 6810 (3) | 1230 (3) | −1629 (3) |
| C(63) | 6638 (3) | 1143 (4) | −2429 (3) |
| C(64) | 6911 (4) | 430 (4) | −2694 (3) |
| C(65) | 7362 (4) | −226 (3) | −2163 (3) |
| C(66) | 7545 (3) | −136 (3) | −1350 (3) |
| C(71) | 6304 (2) | 1483 (3) | 1228 (2) |
| C(72) | 7130 (3) | 1533 (3) | 1818 (3) |
| C(73) | 7284 (3) | 1514 (4) | 2634 (3) |
| C(74) | 6625 (4) | 1455 (4) | 2851 (3) |
| C(75) | 5798 (3) | 1410 (3) | 2264 (3) |
| C(76) | 5633 (3) | 1417 (3) | 1457 (2) |
| C(81) | 5600 (3) | 2565 (3) | −192 (3) |
| C(82) | 4769 (4) | 2686 (4) | −556 (5) |
| C(83) | 4417 (4) | 3497 (5) | −843 (6) |
| C(84) | 4898 (5) | 4172 (5) | −788 (5) |
| C(85) | 5699 (5) | 4090 (4) | −381 (6) |
| C(86) | 6051 (3) | 3274 (4) | −93 (5) |
| H1N[a] | 4891 (31) | 833 (30) | −484 (25) |
| H2N[a] | 5491 (26) | 348 (29) | −411 (24) |

[a] H1N and H2N are bonded to N(6) and were refined in the final cycles.

are presented in Table IV, and an ORTEP drawing of the molecule, together with the atom-numbering scheme, is shown in Figure 1.

The crystal structure of **4** consists of $(Ph_2PN)_2(NSO_2)^-$ anions and $Et_2NH_2^+$ cations, each bonded to two crystallographically independent ions of opposite charge through hydrogen-bonding interactions.[8] Thus, the cation is bonded to the anion via N(4)–H2N---O(1) (N(4)–H2N = 1.00 (8), H2N---O(1) = 1.73 (8), N(4)---O(1) = 2.698 (4) Å; ∠N–H–O = 160 (5)°) and to the anion at $(1 - x, -y, -z)$ via N(4)–H1N---N(1) (N(4)–H1N = 1.11 (8), H1N---N(1) = 1.77 (8), N(1)---N(4) = 2.877 (4) Å; ∠N–H–N = 175 (5)°) to give an extended network of hydrogen bonding.

The anion in **4** can be considered as the hydrolysis product of the mixed phosphazene–sulfanuric ring $(Ph_2PN)_2(NS(O)X)$ where $X = NR_2$.[9] Unlike other $P_2SN_3$ rings of this type, however, which are either boat shaped, $(Cl_2PN)_2(NS(O)Cl)$,[10]

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[8] A related anion, $[(H_2N)_2PN]_2(NSO_2)^-$, has been prepared, but no structural details were reported: Becke-Goehring, M.; Bayer, K.; Mann, T. *Z. Anorg. Allg. Chem.* **1966**, *346*, 143.

[9] For a recent review of mixed phosphazene-sulfanuric ring systems, see: Van de Grampel, J. C. *Rev. Inorg. Chem.* **1981**, *3*, 1.

**Table IV.** Selected Interatomic Distances (Å) and Angles (deg)

| $Et_2NH_2^+[(Ph_2PN)_2(NSO_2)]^-$ | | $(Ph_2PN)_2$-$(NS(O)NPPh_2NPPh_2NH_2)$ | |
|---|---|---|---|
| | | Distances | |
| S-N(1) | 1.613 (3) | S-N(1) | 1.580 (4) |
| S-N(3) | 1.537 (3) | S-N(3) | 1.580 (4) |
| S-O(1) | 1.419 (3) | S-N(4) | 1.585 (4) |
| S-O(2) | 1.399 (3) | S-O | 1.459 (2) |
| N(1)-P(1) | 1.611 (2) | N(1)-P(1) | 1.605 (3) |
| P(1)-N(2) | 1.595 (3) | P(1)-N(2) | 1.600 (4) |
| N(2)-P(2) | 1.605 (3) | N(2)-P(2) | 1.598 (4) |
| P(2)-N(3) | 1.582 (3) | P(2)-N(3) | 1.614 (3) |
| N(4)-C(1) | 1.477 (6) | N(4)-P(3) | 1.592 (3) |
| N(4)-C(3) | 1.490 (5) | P(3)-N(5) | 1.586 (4) |
| C(1)-C(2) | 1.496 (8) | N(5)-P(4) | 1.561 (4) |
| C(3)-C(4) | 1.498 (7) | P(4)-N(6) | 1.625 (3) |
| | | Angles | |
| N(1)-S-N(3) | 112.5 (1) | N(1)-S-N(3) | 112.3 (2) |
| N(1)-S-O(1) | 104.4 (2) | N(1)-S-N(4) | 106.8 (2) |
| N(1)-S-O(2) | 110.6 (2) | N(1)-S-O | 109.1 (2) |
| N(3)-S-O(1) | 108.3 (2) | N(3)-S-N(4) | 109.0 (2) |
| N(3)-S-O(2) | 107.8 (2) | N(3)-S-O | 107.7 (2) |
| O(1)-S-O(2) | 113.1 (2) | N(4)-S-O | 112.0 (2) |
| S-N(1)-P(1) | 119.8 (2) | S-N(1)-P(1) | 121.1 (2) |
| N(1)-P(1)-N(2) | 116.6 (1) | N(1)-P(1)-N(2) | 117.2 (2) |
| P(1)-N(2)-P(2) | 115.8 (1) | P(1)-N(2)-P(2) | 117.4 (2) |
| N(2)-P(2)-N(3) | 117.5 (2) | N(2)-P(2)-N(3) | 115.9 (2) |
| P(2)-N(3)-S | 127.2 (2) | P(2)-N(3)-S | 123.1 (2) |
| C(1)-N(4)-C(3) | 114.9 (4) | S-N(4)-P(3) | 127.2 (2) |
| N(4)-C(1)-C(2) | 111.7 (4) | N(4)-P(3)-N(5) | 123.3 (2) |
| N(4)-C(3)-C(4) | 110.7 (4) | P(3)-N(5)-P(4) | 141.3 (2) |
| | | N(5)-P(4)-N(6) | 116.5 (2) |

or quasi-planar, $(Az_2PN)_2(NSOAz)$ (Az = aziridinyl),[11] the five-atom unit N(1)SN(3)P(2)N(2) in the anion is planar to within 0.05 Å while P(1) lies ca. 0.45 Å out of this plane. The hydrogen bonding to N(1) leads to inequivalence in the S-N bond lengths (S-N(1) = 1.613 (3), S-N(3) = 1.537 (3) Å) and in the angles at N(1) (119.8 (2)°) and N(3) (127.2 (2)°). It may also account for the nonplanarity of the ring (since P(1) is attached to N(1)). The mean P-N bond length of 1.598 (4) Å is comparable to the mean P-N bond distance of 1.597 (6) Å found for $(Ph_2PN)_3$.[12] The geometry about sulfur is essentially tetrahedral, with angles ranging from 104.4 to 113.1°. Hydrogen bonding to O(1) causes slight inequivalence of the S-O bond lengths (1.399 (3), 1.419 (3) Å), for which the mean value of 1.409 (3) Å is close to that found for $S_3N_3O_2^-$ (1.419 (6) Å).[13]

**Crystal and Molecular Structure of 5.** The final atomic coordinates of the non-hydrogen atoms of the molecule are given in Table III. All other parameters and the lists of structure factor amplitudes are available as supplementary material. Selected bond lengths and angles are presented in Table IV, and an ORTEP drawing of the molecule, together with the atom-numbering scheme, is shown in Figure 2. The crystal structure consists of discrete molecular units with no unusual intermolecular contacts.

The molecular structure is found to be a mixed phosphazene–sulfanuric ring of the type $(Ph_2PN)_2(NS(O)R)$ where R is the diphosphazenyl chain, $-NPPh_2NPPh_2NH_2$. The six-membered PNS ring adopts a chair conformation in which S and N(2) are 0.38 and 0.33 Å, respectively, out of the least-squares plane of the central $P_2N_2$ unit. The various conformations found for mixed phosphazene–sulfanuric rings of the type $P_2SN_3$ have been discussed in the previous section. The mean endocyclic P–N bond length of 1.604 (4) Å is not significantly longer than that found for the anion in **4**. The mean S–N bond lengths of 1.582 (4) Å are slightly larger than the mean S–N distance of 1.559 (4) Å found for the structurally related compound **3**, which contains a spirocyclic sulfur atom attached to four nitrogens.[2] Although the exocyclic P–N bond lengths are not equal, they are within the range found for phosphazenyl chains.[14] As would be expected, the terminal P(4)–N(6) bond is significantly longer (1.625 (3) Å) than the other exocyclic P–N bonds, but it is substantially shorter than the single sp$^3$–sp$^3$ P–N bond (in $H_3N^+PO_3^{2-}$)[15]. Interestingly, the conformation of the $-NPPh_2NPPh_2NH_2$ chain is such that an intramolecular hydrogen bond is formed. Values of N(6)–H2N = 0.76 (8), H2N---O = 2.24 (8), and N(6)---O = 2.963 (4) Å and an angle at H2N of 159 (5)° are typical of this type of interaction.[16] Despite this hydrogen bonding, however, the S–O bond distance of 1.459 (2) Å is only slightly longer than that observed in other mixed sulfanuric–phosphazene ring systems (ca. 1.43–1.44 Å).[11] The geometry at sulfur is approximately tetrahedral with bond angles in the range 106.8–112.3°.

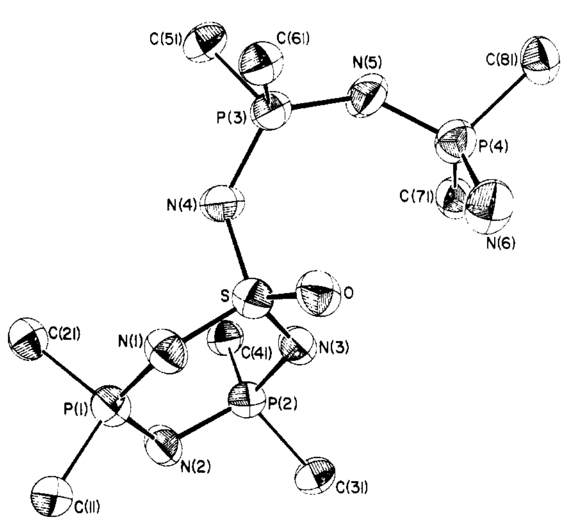

**Figure 2.** ORTEP drawing (50% probability ellipsoids) of $(Ph_2PN)_2(NS(O)NPPh_2NPPh_2NH_2)$ showing the atom-numbering scheme. For clarity only the α-C atoms of the phenyl rings are shown.

**Mechanism of Formation of 4 and 5.** It is interesting to note that the molecular composition of **5** is equivalent to the spirocyclic compound **3** plus one molecule of water. It should be pointed out, however, that **3** is not converted to **5** by aerial hydrolysis. In a separate experiment we have shown that hydrolysis of the twelve-membered ring **2** accounts for the formation of **5**. Similarly, it seems likely that hydrolytic oxidation of the six-membered ring **1**, possibly via $(Ph_2PN)_2(NS(O)NMe_2)$, produces **4**, but we have been unable to confirm the formation of this intermediate.

## Summary and Conclusions

The methods available for the preparation of mixed phosphazene–sulfanuric ring systems have been limited to the use of reagents in which sulfur is in a high oxidation state, e.g. $Cl_3PNSO_2Cl$ or $SO_2(NH_2)_2$, and produce primarily six-membered rings.[9,17] The present results indicate that the oxidation

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(17) There is a brief report of the preparation of the eight-membered ring $(NPCl_2)_3(NSOCl)$: Voswijk, C.; Van de Grampel, J. C. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 120.

and/or hydrolysis of phosphazene–thiazyl systems containing three-coordinate sulfur will provide an alternative route to hybrid ring systems containing four-coordinate sulfur. Since there is a variety of ring sizes available for phosphazene–thiazyl rings (six-[3,18] eight-[19,20] and twelve-membered[1] rings are known), this approach offers the possibility of extending the range of mixed phosphazene–sulfanuric systems to rings larger than six atoms.

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**Supplementary Material Available:** Listings of anisotropic thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, bond lengths and bond angles for phenyl groups, least-squares planes, and observed and calculated structure factors for **4** and **5** (106 pages). Ordering information is given on any current masthead page.

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# The Isomers $F_3CNC$ and $F_3CCN$: Photoelectron Spectra, Thermal Rearrangement, and Effects of Fluorine Substitution on Parent Molecules $C_2H_3N$[§,1,2]

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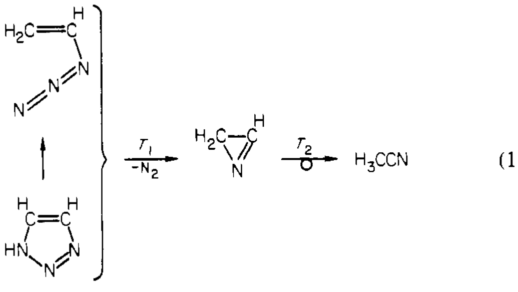
The thermal rearrangement $F_3CNC \rightarrow F_3CCN$ has been monitored by photoelectron (PE) spectroscopy in a gaseous flow system. In contrast to the rather limited stability of liquid $F_3CNC$, the isomerization in the gas phase requires temperatures above 750 K, suggesting a considerable kinetic barrier. MNDO calculations for various compounds $C_2F_3N$ support the assignment of the He I and the He II PE spectra recorded for $F_3CNC$ and $F_3CCN$, allow an estimate of the relative thermodynamical stabilities of the $C_2F_3N$ isomers and, by comparison with the parent species $C_2H_3N$, provide insight into the effects of fluorine substitution $C_2H_3N \leftrightarrow C_2F_3N$ within these six-atom molecules and their radical cations.

## Introduction

The relative stabilities and interconversions of various "valence normal" $C_2H_3N$ isomers have recently been the subject of a number of experimental[3] and theoretical[3-5] investigations. For example, the thermal decompositions of vinyl azide and its isomer, 1,2,3(1*H*)-triazole, monitored by PE spectroscopy, yield 2*H*-azirine as a trappable intermediate which only at higher temperature rearranges to the most stable isomer acetonitrile[3] (eq 1).



(1)

Accompanying MNDO[3] as well as ab initio calculations[4,5] fully reproduce the experimental observations and allow estimates on the unexpectedly high $N_2$ extrusion and isomerization barriers within the six-atom isomer ensemble $C_2H_3N$.

Little information, however, is available on the $C_2F_3N$ ensemble of compounds, where the interest has focused on the two known isomers, trifluoroacetonitrile, $F_3CC{\equiv}N$, and trifluoromethyl isocyanide, $F_3CN{\equiv}C$, and their isomerization.[6] Whereas trifluoroacetonitrile, as acetonitrile itself, is a perfectly stable compound, trifluoromethyl isocyanide exhibits remarkably reduced stability compared to methyl isocyanide, especially in the condensed phase (see Experimental Section). This is in accordance with the lack of data on isocyanides with strong acceptor substituents, especially perfluoroalkyl-substituted ones.

In the following, a combination of photoelectron (PE) spectroscopy and semiempirical MNDO calculations is used to investigate the effects of fluorine substitution on $H_3CN{\equiv}C$ and $H_3CC{\equiv}N$ and to establish the isomer stability sequences for the neutral and positively charged ensembles $C_2X_3N$ with X = H and F. With trifluoromethyl isocyanide predicted to be thermodynamically 130 kJ/mol less stable than trifluoroacetonitrile, the thermal rearrangement

$$F_3CNC \xrightarrow[\circ]{T} F_3CCN \qquad (2)$$

is investigated in a gaseous flow system with use of PE spectroscopic real-time analysis.[3]

## Experimental Section

**Trifluoromethyl isocyanide** has previously been prepared via the reaction of $F_3CNHCF_2Br$ with magnesium,[7] pyrolysis of the imino-

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[§] To the memory of Earl L. Muetterties.
[†] University of Frankfurt.
[‡] Freie Universität Berlin.

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