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A Planar $P_2N_4S_2$ Ring: Preparation and X-ray Structures of $Et_4P_2N_4S_2Cl_2$ and $[R_4P_2N_4S_2][AlCl_4]_2$ (R = Et, Ph)

Michele Brock, Tristram Chivers,*
Masood Parvez, and Rainer Vollmerhaus

Department of Chemistry, The University of Calgary,
Calgary, Alberta, Canada T2N 1N4

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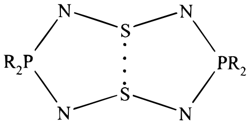
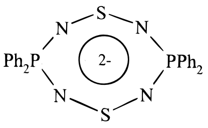
Introduction

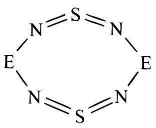
The 10 π-electron systems 1,5-$R_4P_2N_4S_2$, **1a**−**c**,[1] adopt folded structures with transannular S···S distances of 2.50−2.55 Å. A characteristic reaction of these inorganic heterocycles is the oxidative addition of halogens to give, in the case of **1b**, $Ph_4P_2N_4S_2X_2$ (X = Cl, Br).[2a] The $P_2N_4S_2$ ring in $Ph_4P_2N_4S_2Br_2$ has a chair structure, with planar PNP units and the sulfur atoms on either side of this plane, and essentially equal S−Br bond lengths.[2] The ring system **1b** may also be reduced to the corresponding dianion $Ph_4P_2N_4S_2^{2-}$ by 2 molar equiv of $M[BEt_3H]$ (M = Li,[3] Na,[4] K[4]), but the structure of the 12 π-electron dianion in the insoluble alkali metal derivatives is unknown. The reagents **1** and **2** have been used to prepare a variety of coordination complexes of the $P_2N_4S_2$ ring with transition metals either by oxidative addition reactions of **1**[4−6] or by metathetical reactions of the dianion **2**.[4,6,7]



1a, R = Et[1a]
1b, R = Ph[1b]
1c, R = Me[1c]



2



3

A large number of eight-membered sulfur diimide derivatives of the type **3** (E = B,[8] Si,[9] P(III),[10] As,[11] Sb[12]) have been structurally characterized. In the majority of cases the $E_2N_4S_2$ ring assumes a boat conformation, but there are two examples in which a planar structure is adopted, apparently for steric reasons [E = Si^tBu_2,[9a] $P(N^iPr_2)[Cr(CO)_5]$ [10]]. It was of interest, therefore, to prepare the eight π-electron dication $R_4P_2N_4S_2^{2+}$ (**3**, E = PR_2^+) for structural comparisons.

Experimental Section

Reagents and General Procedures. 1,5-$Et_4P_2N_4S_2$[1a] and $Ph_4P_2N_4S_2Cl_2$[2a] [$\delta(^{31}P)(CH_2Cl_2)$ +2.3 ppm] were prepared by the literature methods. Commercial SO_2Cl_2 and Al_2Cl_6 were purified by distillation and sublimation, respectively. Solvents were dried with the appropriate drying agents and distilled immediately before use. All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of dry nitrogen or argon.

Instrumentation. ^{27}Al and $\{^1H\}^{31}P$ NMR spectra were recorded on a Bruker AM-400 spectrometer. Chemical shifts are given relative to $Al(NO_3)_3$ in D_2O and 85% H_3PO_4. Elemental analyses were provided by the Canadian Microanalytical Service, Vancouver, BC, Canada, and by the Analytical Services Laboratory, Department of Chemistry, The University of Calgary. Infrared spectra were obtained on a Mattson 4030 FTIR spectrophotometer.

Preparation of $Et_4P_2N_4S_2Cl_2$ (4a). Neat SO_2Cl_2 (0.202 g, 1.50 mmol) was added dropwise, by syringe, to a stirred solution of 1,5-$Et_4P_2N_4S_2$ (0.449 g, 1.50 mmol) in CH_2Cl_2 (20 mL) at 23 °C. The initial addition produces a red solution which reverts to a pale yellow when a stoichiometric amount of SO_2Cl_2 has been added. After 1 h, the solvent and volatile products were removed by vacuum to give a yellow solid, which was recrystallized from acetonitrile (∼10 mL) to give pale yellow crystals of $Et_4P_2N_4S_2Cl_2$ (0.325 g, 0.880 mmol, 59%). Anal. Calcd for $C_8H_{20}N_4P_2S_2Cl_2$: C, 26.02; H, 5.46; N, 15.17. Found: C, 25.71; H, 5.63; N, 14.74. IR (Nujol, cm^{-1}): 1274 w, 1217 s, 1172 s, 1085 m, 1019 m, 999 w, 981 w, 777 s, 742 m, 727 w, 666 w, 459 m, 406 m, 383 w, 365 w, 358 w, 341 w, 313 w, 279 m, 246 m, 225 m, 206 s. NMR spectra (δ, ppm) (CD_2Cl_2): $\{^1H\}^{31}P$ 27.4. ^1H 1.25 [d of t, $^3J(^1H{-}^{31}P) = 20.9$ Hz, $^3J(^1H{-}^1H) = 7.6$ Hz], 2.26 [d of q, $^3J(^1H{-}^{31}P) = 14.8$ Hz, $^3J(^1H{-}^1H) = 7.4$ Hz].

When a sample of **4a** is heated to 80 °C it turns orange; at 85 °C it becomes red and then deepens in color until it melts at 115−116 °C.

Preparation of $[Et_4P_2N_4S_2][AlCl_4]_2$ (5a). Solid aluminum chloride (0.723 g, 5.42 mmol) was added to a stirred solution of $Et_4P_2N_4S_2Cl_2$ (1.00 g, 2.71 mmol) in CH_2Cl_2 (20 mL) at 23 °C. A yellow precipitate of $[Et_4P_2N_4S_2][AlCl_4]_2$ (1.04 g, 1.63 mmol, 60%) was separated by filtration. Anal. Calcd for $C_8H_{20}N_4Al_2Cl_8S_2$: C, 15.11; H, 3.17; N, 8.81. Found: C, 14.26; H. 3.26; N, 8.24. ^1H NMR (THF): δ (ppm) 1.23 [d of t, $^3J(^1H{-}^3P) = 20.8$ Hz, $^3J(^1H{-}^1H) = 7.6$ Hz], 2.28 [d of q, $^2J(^1H\text{-}^{31}P) = 14.8$ Hz, $^3J(^1H{-}^1H) = 7.5$ Hz]. $\{^1H\}^{31}P$ NMR (CH_2Cl_2): δ (ppm) 32.2, ^{27}Al NMR (CH_2Cl_2): δ (ppm) 102.4. IR (Nujol, cm^{-1}): 1340 s, 1330 s, 1241 s, 1224 m, 1098 w, 1038 m, 989 w, 774 m, 741 w, 734 s, 502 vs, 462 vs, 398 vs

Preparation of $[Ph_4P_2N_4S_2][AlCl_4]_2$ (5b). Orange crystals of $[Ph_4P_2N_4S_2][AlCl_4]_2$ were obtained in 29% yield from the reaction of $Ph_4P_2N_4S_2Cl_2$ (0.146 g, 0.260 mmol) and $AlCl_3$ (0.069 g, 0.520 mmol) by using a procedure similar to that described for the preparation of **5a**. Anal. Calcd for $C_{24}H_{20}N_4Al_2Cl_8S_2$: C, 34.81; H, 2.43; N, 6.77. Found: C, 34.85; H, 3.46; N, 6.47. $\{^1H\}^{31}P$ NMR (CH_2Cl_2): δ (ppm) 7.3. ^{27}Al NMR (CH_2Cl_2): δ (ppm) 102.8. IR (cm^{-1}): 1260 vs, 1120 m, 1101 m, 899 w, 796 m, 619 m, 504 m.

X-ray Analyses. All measurements were made on a Rigaku AFC6S diffractometer using the $\omega - 2\theta$ technique and Mo Kα radiation. A colorless block of **4a** was obtained by recrystallization from acetonitrile at −20 °C. Pale yellow prisms of **5a** and **5b** were formed in CH_2Cl−hexanes and CH_2Cl_2 solutions, respectively, at 23 °C. Crystals were

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Table 1. Crystallographic Data for **4a**, **5a**, and **5b**

	4a	**5a**	**5b**
formula	$C_8H_{20}N_4P_2S_2Cl_2$	$C_8H_{20}N_4P_2S_2Cl_8Al_2$	$C_{25}H_{22}N_4P_2S_2Cl_{10}Al_2$
fw	369.25	635.92	913.04
cryst size, mm^3	0.80 × 0.60 × 0.40	0.25 × 0.18 × 0.12	0.26 × 0.20 × 0.12
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	8.417(5)	8.589(1)	14.453(5)
b, Å	13.456(6)	10.991(1)	15.320(5)
c, Å	8.130(4)	7.574(2)	9.890(2)
α, deg	99.32(4)	110.04(1)	108.82(2)
β, deg	113.64(4)	96.75(1)	93.47(2)
γ, deg	96.58(4)	98.13(1)	69.47(2)
V, Å^3	815.8(9)	654.3(2)	1937(1)
Z	2	1	2
T, °C	−103	−103	−73
λ, Å	0.71069	0.71069	0.71069
ρ_{calcd}, g cm^{-3}	1.503	1.614	1.565
μ, cm^{-1}	8.39	12.13	9.80
2θ range (deg)	4−50	2−40	2−50
scan speed (deg min^{-1})	16	4	4
no. of unique data	2822	1704	6896
no. of obsd data	2373^a	1143^a	1186^a
no. of parms refined	163	118	281
R^b	0.030	0.047	0.055
$R_w{}^c$	0.039	0.058	0.046
goodness of fit	2.28	2.45	1.43
max/min resid dens (ρ A^{-3})	0.37/−0.36	0.53/−0.47	0.46/−0.39

^{a} $I > 3\sigma(I)$. ^{b} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{c} $R_w = \sqrt{(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o{}^2)}]$.

Table 2. Atomic coordinates and B_{eq} for **4a**

atom	x	y	z	$B_{eq}{}^a$
Cl(1)	−0.0957(1)	0.05387(6)	0.2732(1)	2.94(2)
Cl(2)	0.5694(1)	0.34197(7)	0.9125(1)	3.45(2)
S(1)	−0.07267(9)	0.22390(6)	0.30846(10)	1.80(1)
S(2)	0.35791(10)	0.18248(6)	0.74675(10)	1.93(2)
P(1)	0.29825(9)	0.21838(6)	0.38265(10)	1.58(2)
P(2)	0.04808(9)	0.28493(6)	0.70067(10)	1.58(1)
N(1)	0.1202(3)	0.2635(2)	0.3364(3)	1.93(5)
N(2)	−0.1001(3)	0.2568(2)	0.4850(3)	1.89(5)
N(3)	0.1929(3)	0.2125(2)	0.7618(3)	1.89(5)
N(4)	0.3640(3)	0.1638(2)	0.5583(3)	1.87(5)
C(1)	0.4696(4)	0.3262(2)	0.4325(4)	2.33(7)
C(2)	0.4256(5)	0.3894(3)	0.2864(5)	3.44(8)
C(3)	0.2812(4)	0.1241(2)	0.1904(4)	2.05(6)
C(4)	0.4484(4)	0.0824(3)	0.2186(5)	3.52(8)
C(5)	0.1527(4)	0.4175(2)	0.7606(4)	2.45(7)
C(6)	0.0228(5)	0.4904(3)	0.7378(5)	3.53(8)
C(7)	−0.0765(4)	0.2666(2)	0.8300(4)	2.24(7)
C(8)	−0.1650(4)	0.1555(3)	0.7929(5)	2.84(8)

^{a} $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos α)$.

Table 3. Atomic Coordinates and B_{eq} for **5a**

atom	x	y	z	$B_{eq}{}^a$
Cl(1)	−0.061(3)	0.1088(2)	−0.0251(3)	2.86(6)
Cl(2)	−0.2077(3)	0.1795(2)	0.4679(3)	2.78(6)
Cl(3)	−0.0301(3)	0.3906(2)	0.2522(4)	3.11(6)
Cl(4)	−0.4305(3)	0.3716(2)	0.3039(3)	2.53(6)
S(1)	−0.3049(3)	0.4310(2)	0.8697(3)	2.13(6)
P(1)	−0.6602(3)	0.3184(2)	0.8133(3)	1.71(5)
Al(1)	−0.2411(3)	0.2597(3)	0.2490(4)	1.98(6)
N(1)	−0.4682(8)	0.3427(6)	0.8024(9)	1.8(2)
N(2)	−0.2757(8)	0.5647(7)	1.0286(10)	1.8(2)
C(1)	−0.7093(11)	0.1743(8)	0.8687(12)	2.1(2)
C(2)	−0.8873(11)	0.1299(9)	0.8536(13)	2.6(2)
C(3)	−0.7645(11)	0.2962(9)	0.5864(13)	2.6(2)
C(4)	−0.7491(11)	0.1708(9)	0.4270(13)	2.9(2)

^{a} $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos α)$.

Table 4. Atomic coordinates and B_{eq} for **5b**

atom	x	y	z	B_{eq}
Cl(1)	0.2863(6)	0.7133(6)	0.620(1)	10.2(4)
Cl(2)	0.1984(6)	0.6539(5)	0.8816(8)	7.7(3)
Cl(3)	0.2109(4)	0.5122(5)	0.5261(7)	4.6(2)
Cl(4)	0.4268(4)	0.5016(5)	0.7070(7)	4.4(2)
Cl(5)	0.8536(4)	−0.0914(4)	0.5800(7)	4.0(2)
Cl(6)	0.7855(4)	0.0902(5)	0.9052(7)	4.1(2)
Cl(7)	0.6767(5)	0.1390(5)	0.6019(7)	4.5(2)
Cl(8)	0.6157(5)	−0.0197(5)	0.7267(7)	5.2(2)
Cl(9)	0.0635(5)	0.3305(5)	0.3626(8)	6.2(2)
Cl(10)	0.0869(7)	0.4119(6)	0.1469(8)	8.1(3)
S(1)	0.6288(4)	0.3883(4)	0.8730(7)	2.7(2)
S(2)	0.9620(4)	0.1244(4)	0.1907(7)	2.6(2)
P(1)	0.5619(5)	0.6089(4)	1.0071(7)	2.3(2)
P(2)	0.9394(4)	−0.0739(5)	0.1028(7)	2.3(2)
Al(1)	0.282(6)	0.5957(6)	0.6809(9)	4.3(2)
Al(2)	0.7323(5)	0.0294(5)	0.7041(8)	3.0(2)
N(1)	0.625(1)	0.495(1)	0.918(2)	2.1(5)
N(2)	0.545(1)	0.362(1)	0.912(2)	2.4(5)
N(3)	0.934(1)	0.040(1)	0.190(2)	2.6(5)
N(4)	1.015(1)	0.123(1)	0.063(2)	2.3(5)
C(1)	0.643(2)	0.645(1)	1.142(2)	2.2(5)
C(2)	0.743(2)	0.605(2)	1.110(3)	4.4(6)
C(3)	0.801(2)	0.644(2)	1.216(3)	5.4(7)
C(4)	0.760(2)	0.717(2)	1.332(3)	4.0(6)
C(5)	0.660(2)	0.761(2)	1.366(3)	4.7(6)
C(6)	0.598(2)	0.724(2)	1.266(3)	3.3(5)
C(7)	0.537(1)	0.676(1)	0.890(2)	1.6(5)
C(8)	0.590(1)	0.641(1)	0.759(2)	2.3(5)
C(9)	0.575(2)	0.699(2)	0.668(3)	6.1(7)
C(10)	0.503(2)	0.787(2)	0.709(3)	3.6(6)
C(11)	0.451(2)	0.827(2)	0.833(3)	3.8(6)
C(12)	0.466(2)	0.768(2)	0.924(2)	3.0(5)
C(13)	1.011(1)	−0.152(1)	0.199(2)	1.9(5)
C(14)	1.051(2)	−0.121(2)	0.323(3)	3.4(6)
C(15)	1.098(2)	−0.184(2)	0.403(3)	4.5(6)
C(16)	1.106(2)	−0.279(2)	0.345(3)	3.8(6)
C(17)	1.066(2)	−0.313(2)	0.224(3)	5.5(7)
C(18)	1.015(2)	−0.247(2)	0.150(3)	4.4(6)
C(19)	0.819(2)	−0.075(1)	0.101(2)	2.7(5)
C(20)	0.762(2)	−0.038(2)	0.227(2)	2.5(5)
C(21)	0.673(2)	−0.051(2)	0.233(2)	3.6(6)
C(22)	0.639(2)	−0.102(2)	0.115(3)	3.8(6)
C(23)	0.693(2)	−0.142(2)	−0.012(3)	4.6(6)
C(24)	0.783(2)	−0.129(2)	−0.016(2)	3.6(6)
C(25)	0.024(2)	0.426(2)	0.297(3)	6.1(7)

^{a} $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos α)$.

mounted in a glass capillary (**4a**, **5a**) or on a glass fiber coated with epoxy (**5b**). Crystal data and processing parameters for **4a**, **5a** and **5b** are given in Table 1.

The data were corrected for Lorentz and polarization effects. The positional parameters are given in Tables 2−4. The structures were solved by direct methods (**4a**[14a], **5a**[14b], **5b**[14b]) and expanded using Fourier techniques.[15] The non-H atoms of **4a** and **5a** were refined anisotropically. For **5b**, the carbon atoms were allowed isotropic temperature factors and the unit cell contained one molecule of CH_2Cl_2 per formula unit. Hydrogen atoms were included at geometrically idealized

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positions with C−H 0.95 Å and were not refined. In the refinement cycles, weights were derived from counting statistics. Scattering factors were those of Cromer and Waber,[16] and allowance was made for anomalous dispersion.[17] All calculations were performed using teXsan.[18]

Results and Discussion

Synthesis of $Et_4P_2N_4S_2Cl_2$ and $[Et_4P_2N_4S_2][AlCl_4]_2$. The *S,S′*-dichloro derivative **4a** was prepared, in a manner similar to that described for $Ph_4P_2N_4S_2Cl_2$,[2a] by the oxidative addition of Cl_2 (as SO_2Cl_2) to 1,5-$Et_4P_2N_4S_2$ in dichloromethane at 23 °C (eq 1). Compound **4a** is a moisture-sensitive, pale yellow

$$Et_4P_2N_4S_2 + SO_2Cl_2 \xrightarrow{-SO_2} Et_4P_2N_4S_2Cl_2 \qquad (1)$$

solid. An excess of the chlorinating agent should be avoided since it will give rise to the thermally unstable trichloride salt $[Et_4P_2N_4S_2Cl][Cl_3]$ (cf. $[(Me_2N)_2C_2N_4S_2Cl][Cl_3]$).[19] The chlorination reaction is readily monitored by observing the disappearance of the characteristic ^{31}P NMR resonance at 136.1 ppm for 1,5-$Et_4P_2N_4S_2$[1a] and the appearance of a new signal at 27.4 ppm for **4a**. The treatment of **4a** or **4b** with 2 molar equiv of $AlCl_3$ in CH_2Cl_2 at 23 °C produces $[R_4P_2N_4S_2][AlCl_4]_2$ (**5a**, R = Et; **5b**, R = Ph) as orange, moisture sensitive crystals (eq 2). The ^{31}P NMR resonances of **4a** and **4b** are shifted ∼5

$$\begin{array}{ccc} R_4P_2N_4S_2Cl_2 + 2AlCl_3 & \rightarrow & [R_4P_2N_4S_2][AlCl_4]_2 \qquad (2) \\ \mathbf{4a}, R = Et & & \mathbf{5a}, R = Et \\ \mathbf{4b}, R = Ph & & \mathbf{5b}, R = Ph \end{array}$$

ppm to high frequency upon formation of the corresponding dications $R_4P_2N_4S_2^{2+}$. The ^{27}Al NMR spectra of **5a** and **5b** exhibit singlets at ∼103 ppm, characteristic of the $AlCl_4^-$ counterion.[20]

Crystal and Molecular Structure of $Et_4P_2N_4S_2Cl_2$. Two aspects of the structure of **4a** are of interest in comparison to those of other *S,S′*-disubstituted derivatives of the $P_2N_4S_2$ ring.[21] The first concerns the conformation of the eight-membered ring. Figure 1 shows an ORTEP drawing of **4a** with the atomic numbering scheme. In contrast to the long chair conformation of the $P_2N_4S_2$ ring in $Ph_4P_2N_4S_2Br_2$,[2] in which the two P and four N atoms are almost planar and the S atoms lie ∼0.5 Å out (and on opposite sides) of this plane, the eight-membered ring in **4a** is best described as a distorted boat with the phosphorus atoms in the prow and stern positions. The orientation and length of the exocyclic S−Cl bonds in **4a** provide the second focus of interest. The pertinent bond lengths and bond angles are given in Table 5. The structure of **4a** resembles that of $Ph_4P_2N_4S_2Br_2$[2] in that the S−Cl bonds adopt a *trans* (*axial*, *axial*) arrangement. However, there is a substantial difference (∼0.28 Å) in the S−Cl bond distances for **4a** whereas the S−Br bond lengths in $Ph_4P_2N_4S_2Br_2$ are equal.[2] The values of 2.235(1) and 2.419(1) Å for S(1)−Cl(1) and S(2)−Cl(2), respectively, may be compared with the corresponding S−Cl distance of 2.18 Å for $S_4N_4Cl_2$.[22] These data imply a tendency toward ionization of the S(2)−Cl(2) bond, cf. 2.357(2) Å for d(S−Cl) in the lower homologue $Ph_4P_2N_3SCl$ for which significant ionic character has been invoked.[23] The structure of **4a** is reminiscent of those previously reported for the salts $[(Me_2N)_2C_2N_4S_2Cl][X]$.[19] Although the structure for the *S,S′*-dichloro derivative (X = Cl) is unknown,[24] the $(Me_2N)_2C_2N_4S_2Cl^+$ cation in the Cl_3^- salt exhibits an S−Cl distance of 2.290(3) Å and weak (S···Cl) interactions involving the cationic sulfur center (Figure 2).[19] For comparison, the corresponding interactions in **4a** are also illustrated in Figure 2. Thus the structure of **4a** can be thought to involve an incipient $Et_4P_2N_4S_2Cl^+$ cation, and it provides further support for the proposed polar reaction pathway for the oxidation of dithiatetrazocines by halogens.[19]

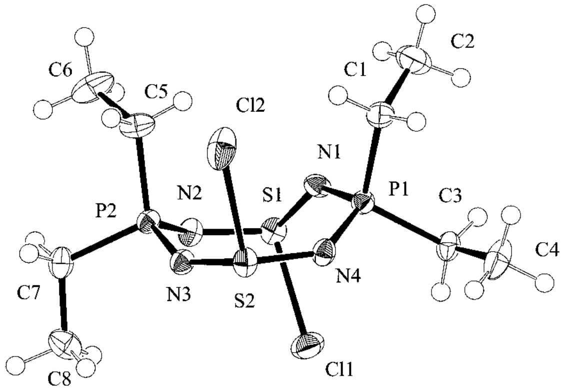

Figure 1. ORTEP diagram and atomic numbering scheme for $Et_4P_2N_4S_2Cl_2$ (**4a**).

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for $Et_4P_2N_4S_2Cl_2$ (**4a**)

Bond Distances			
Cl(1)−S(1)	2.235(1)	Cl(2)−S(2)	2.419(1)
S(1)−N(1)	1.561(3)	S(1)−N(2)	1.547(2)
S(2)−N(3)	1.535(3)	S(2)−N(4)	1.535(2)
P(1)−N(1)	1.608(3)	P(1)−N(4)	1.638(2)
P(2)−N(2)	1.642(2)	P(2)−N(3)	1.621(2)
P(1)−C(1)	1.792(3)	P(1)−C(3)	1.791(3)
P(2)−C(5)	1.792(3)	P(2)−C(7)	1.781(3)
Bond Angles			
Cl(1)−S(1)−N(1)	104.06(9)	Cl(1)−S(1)−N(2)	103.3(1)
N(1)−S(1)−N(2)	112.8(1)	Cl(2)−S(2)−N(3)	100.1(1)
Cl(2)−S(2)−N(4)	102.8(1)	N(3)−S(2)−N(4)	119.3(1)
N(1)−P(1)−N(4)	117.6(1)	N(1)−P(1)−C(1)	105.6(1)
N(1)−P(1)−C(3)	111.6(1)	N(4)−P(1)−C(1)	107.1(1)
N(4)−P(1)−C(3)	105.3(1)	C(1)−P(1)−C(3)	109.5(1)
N(2)−P(2)−N(3)	118.0(1)	N(2)−P(2)−C(5)	108.5(1)
N(2)−P(2)−C(7)	104.7(1)	N(3)−P(2)−C(5)	111.3(1)
N(3)−P(2)−C(7)	104.4(1)	C(5)−P(2)−C(7)	109.4(1)
S(1)−N(1)−P(1)	136.6(2)	S(1)−N(2)−P(2)	128.3(2)
S(2)−N(3)−P(2)	144.8(2)	S(2)−N(4)−P(1)	134.7(2)

The unequal S−Cl bond distances give rise to significant differences in the geometrical parameters of the NSN units on opposite sides of the $P_2N_4S_2$ ring in **4a**. Thus the mean S−N bond lengths involving the incipient cationic center S(2) are 1.535(3) Å compared to 1.554(3) Å for S(1)−N and the corresponding NSN bond angles are 119.3(1) and 112.8(1)°, respectively. There is a wide variation in the endocyclic bond angles at the four nitrogen atoms, which fall within the range

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Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for $[Et_4P_2N_4S_2][AlCl_4]_2$ (**5a**) and $[Ph_4P_2N_4S_2][AlCl_4]_2$ (**5b**)[a]

Bond Distances

5a		**5b**			
		molecule A		molecule B	
S(1)−N(1)	1.509(7)	S(1)−N(1)	1.53(2)	S(2)−N(3)	1.48(2)
S(1)−N(2)	1.511(7)	S(1)−N(2)	1.50(2)	S(2)−N(4)	1.51(2)
P(1)−N(1)	1.650(7)	P(1)−N(1)	1.63(2)	P(2)−N(3)	1.65(2)
P(1)−N(2*)	1.639(7)	P(1)−N(2*)	1.64(2)	P(2)−N(4**)	1.64(2)
P(1)−C(1)	1.781(9)	P(1)−C(1)	1.80(2)	P(2)−C(13)	1.77(2)
P(1)−C(3)	1.762(9)	P(1)−C(7)	1.73(2)	P(2)−C(19)	1.74(2)
Cl(1)−Al(1)	2.116(4)	Cl(1)−Al(1)	2.091(10)	Cl(5)−Al(2)	2.127(9)
Cl(2)−Al(1)	2.138(3)	Cl(2)−Al(1)	2.15(1)	Cl(6)−Al(2)	2.129(9)
Cl(3)−Al(1)	2.141(4)	Cl(3)−Al(1)	2.133(9)	Cl(7)−Al(2)	2.131(9)
Cl(4)−Al(1)	2.169(4)	Cl(4)−Al(1)	2.128(9)	Cl(8)−Al(2)	2.121(9)

Bond Angles

5a		**5b**			
		molecule A		molecule B	
N(1)−S(1)−N(2)	121.6(4)	N(1)−S(1)−N(2)	122.0(9)	N(3)−S(2)−N(4)	121.7(10)
N(1)−P(1)−N(2*)	117.6(3)	N(1)−P(1)−N(2*)	120.7(8)	N(3)−P(2)−N(4**)	117.8(9)
S(1)−N(2)−P(1*)	151.2(5)	S(1)−N(1)−P(1)	145(1)	S(2)−N(3)−P(2)	147(1)
S(1)−N(1)−P(1)	149.6(5)	S(1)−N(2)−P(1*)	151(1)	S(2)−N(4)−P(2*)	152(1)
N(1)−P(1)−C(1)	108.6(4)	N(1)−P(1)−C(1)	104.1(9)	N(3)−P(2)−C(13)	108.5(9)
N(1)−P(1)−C(3)	106.7(4)	N(1)−P(1)−C(7)	108.0(10)	N(3)−P(2)−C(19)	107.5(10)
N(2*)−P(1)−C(1)	105.8(4)	N(2*)−P(1)−C(1)	107.7(9)	N(4**)−P(2)−C(13)	107.5(10)
N(2*)−P(1)−C(3)	107.4(4)	N(2*)−P(1)−C(7)	104.7(9)	N(4**)−P(2)−C(19)	106(1)
C(1)−P(1)−C(3)	110.7(4)	C(1)−P(1)−C(7)	111.6(9)	C(13)−P(2)−C(19)	108.5(10)
Cl(1)−Al(1)−Cl(2)	111.3(1)	Cl(1)−Al(1)−Cl(2)	108.6(5)	Cl(5)−Al(2)−Cl(6)	107.2(4)
Cl(1)−Al(1)−Cl(3)	108.4(2)	Cl(1)−Al(1)−Cl(3)	109.7(4)	Cl(5)−Al(2)−Cl(7)	110.9(4)
Cl(1)−Al(1)−Cl(4)	109.6(2)	Cl(1)−Al(1)−Cl(4)	112.9(4)	Cl(5)−Al(2)−Cl(8)	109.7(4)
Cl(2)−Al(1)−Cl(3)	111.9(2)	Cl(2)−Al(1)−Cl(3)	107.8(4)	Cl(6)−Al(2)−Cl(7)	109.4(4)
Cl(2)−Al(1)−Cl(4)	107.4(2)	Cl(2)−Al(1)−Cl(4)	108.2(4)	Cl(6)−Al(2)−Cl(8)	112.1(4)
Cl(3)−Al(1)−Cl(4)	108.2(1)	Cl(3)−Al(1)−Cl(4)	109.6(4)	Cl(7)−Al(2)−Cl(8)	107.7(4)

[a] Symmetry codes: (*) 1 − x, 1 − y, 2 − z; (**) 2 − x, −y, −z.

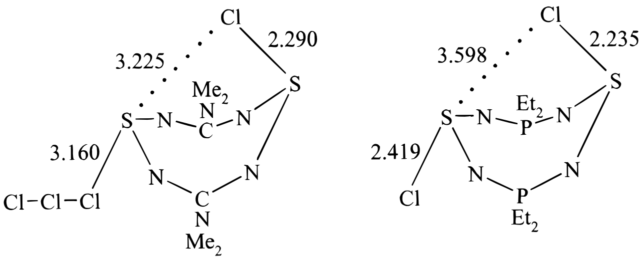

Figure 2. Schematic representation of S−Cl interactions in $[(Me_2N)_2C_2N_4SCl][Cl_3]$ and $Et_4P_2N_4S_2Cl_2$.

128.3(2)−144.8(2)°. The mean P−N distance of 1.627(3) Å [range 1.608(3)−1.642(2)°] is not significantly different from the value of 1.616(8) Å found for the parent ring system **1a**.[1a] The mean NPN bond angle in **4a** is, however, substantially larger than that in **1a** [117.8(1) vs 109.8(4)°[1a]] presumably owing to the loss of the constraining influence of the transannular S···S interaction in **1a**.

The markedly different S−Cl bond distances should give rise to two characteristic S−Cl stretching vibrations in the IR spectrum of **4a**. On the basis of a recent correlation between ν(S−Cl) and d(S−Cl) reported by Passmore et al.,[25] we tentatively assign the IR bands at 358 and 225 cm^{-1} to S−Cl stretches.

Crystal and Molecular Structures of $[R_4P_2N_4S_2][AlCl_4]_2$ (5a, R = Et; 5b, R = Ph). The X-ray structural determinations showed that **5a** and **5b** consist of noninteracting, planar $R_4P_2N_4S_2^{2+}$ cations and tetrahedral $AlCl_4^-$ anions. Figure 3 shows an ORTEP drawing and the atomic numbering scheme for the dication in **5a**. Pertinent bond distances and bond angles for **5a** and **5b** are given in Table 5. The $Et_4P_2N_4S_2^{2+}$ cation represents only the third example of a planar ring system of the type **3**. In the other two cases (E = Si^{t}Bu$_2$,[9a] P(N^{i}Pr$_2$)[Cr(CO)$_5$][10]), the planarity is apparently enforced by the steric bulk of the substituents E in these eight-membered rings. In the present examples (E = Et_2P^+, Ph_2P^+), however, steric constraints do not provide a plausible explanation of planarity. On the other hand, the metrical parameters for $Et_4P_2N_4S_2^{2+}$ supply no evidence for the delocalized π-bonding that might be expected to ensue from the combination of planarity and the

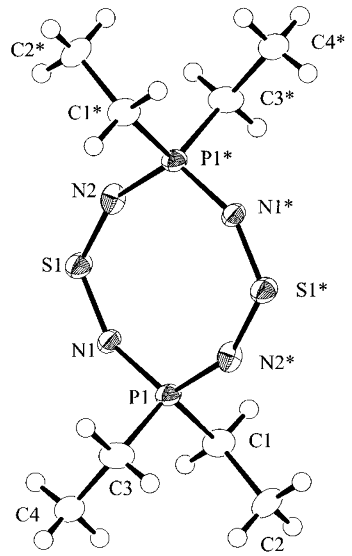

Figure 3. ORTEP diagram and atomic numbering scheme for the cation in $[Et_4P_2N_4S_2][AlCl_4]_2$ (**5a**).

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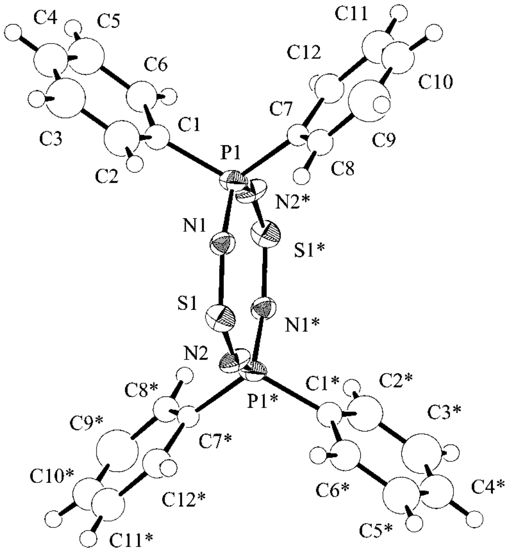
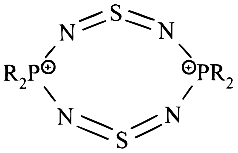


Figure 4. ORTEP diagram and atomic numbering scheme for the $Ph_4P_2N_4S_2^{2+}$ cation in molecule A of **5b**. For molecule B, P(1) becomes P(2), S(1) becomes S(2), and N(1) and N(2), are N(3) and N(4).

2+ charge. The mean S−N distances of 1.510(7) Å are typical for localized *Z*,*Z* sulfur diimide (−N=S=N−) groups[26] consistent with the valence bond representation illustrated below (cf. d(S−N) = 1.55 Å in the delocalized, ten π-electron dication $S_4N_4^{2+}$).[27] Surprisingly, the mean P−N bond length of 1.645(7) Å is somewhat longer than the corresponding value of 1.616(8) Å reported for the neutral ring system **1a**.[1a] The mean endocyclic bond angles at S and N in $Et_4P_2N_4S_2^{2+}$ are 121.6(4) and 150.4(5)°, respectively. The large value of the latter is presumably enforced by the planarity of the eight-membered ring (cf. 147.2° in $N_4P_4F_8$).[28]



The unit cell of **5b** contains two different $Ph_4P_2N_4S_2^{2+}$ cations which differ with respect to the different orientations of the two Ph groups attached to the same phosphorus atom. This difference is manifested in a disparity of ∼30° in the torsion angles C(1)−P(1)−C(7)−C(8) vs C(13)−P(2)−C(19)−C(20) [96(1) vs 64(2)°] and C(6)−C(1)−P(1)−C(7) vs C(18)−C(13)−P(2)−C(19) [87(1) vs 57(2)°]. An ORTEP diagram of one of the $Ph_4P_2N_4S_2^{2+}$ cations is illustrated in Figure 4. Although the quality of the X-ray structure of **5b** is relatively poor, it is clear from the data given in Table 6 that the $Ph_4P_2N_4S_2^{2+}$ cation exhibits the same structural trends as observed for $Et_4P_2N_4S_2^{2+}$.

The dications $R_4P_2N_4S_2^{2+}$ (R = Et, Ph) provide an alternative to **1** and **2** for the synthesis of transition metal complexes of the $P_2N_4S_2$ ring, e.g., by reaction with metal carbonyl anions.

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Supporting Information Available: Tables giving X-ray experimental details, atomic coordinates for hydrogen atoms, anisotropic thermal parameters, bond distances, bond angles, and torsion angles (22 pages). Ordering information is given on any current masthead page.

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