similar to the above has been given for the very long U–C bond lengths in the phosphoylide complex $(C_5H_5)U[(CH_2)(CH_2)PPh_2]$.[53]

Alternatively, the Li–S bond elongation may be interpreted by the larger coordination number of **2**. Thus, also longer are the Li–O distances of 2.154 Å (average) relative to 2.06 Å (average) for **1**, albeit the difference is less significant in this case. Within the LiS_2O_4 coordination sphere of **2**, the Li–O(2,4) bond lengths trans to sulfur atoms are shorter by 0.11 Å (average) than the Li–O(1,3) distances as a consequence of the weak Li–S coordination.

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Supplementary Material Available: For **1** and **2**, tables of crystal data (Table S1), complete anisotropic and isotropic temperature factors of non-hydrogen atoms (Tables S2 and S5), and hydrogen atom parameters (Tables S3 and S6) (5 pages); listings of observed and calculated structure factors (Tables S4 and S6) (22 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada, and University of New Brunswick, Fredericton, New Brunswick E3B 6E2, Canada

Experimental Evidence for Comparable Strength of P–S and P–N pπ-Bonding within the Heteronaphthalenic Framework: Spectroscopic and Structural Studies of the 1,3,2-Benzazathiaphospholium System as a Cation and as Neutral Halides

Neil Burford,*[,1a] Anne I. Dipchand,[1a] Bruce W. Royan,[1a] and Peter S. White[1b]

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The new heteronaphthalenic framework 1,3,2-benzazathiaphospholium has been prepared as a free cation **1**[NSP] and as the neutral chloride **2**[NSPCl] and bromide **2**[NSPBr] derivatives. The spectroscopic and structural (crystal data for $C_6H_5AlCl_4NPS$: monoclinic, $P2_1/c$, $a = 6.4773$ (6) Å, $b = 23.5434$ (21) Å, $c = 8.5101$ (6) Å, $\beta = 98.048$ (7)°, $Z = 4$) features of the cation are consistent with a hybrid of the corresponding dithia **1**[S_2P] and diamino **1**[N_2P] derivatives. In particular, the P–N and P–S bond lengths are very similar to those of the parent cations and represent experimental evidence for P–N and P–S pπ-bonding of comparable strength, in agreement with the theoretical π-bond energies. The neutral halides, 2-chloro-1,3,2-benzazathiaphosphole (crystal data for C_6H_5ClNPS: monoclinic, $P2_1/c$, $a = 8.5607$ (10) Å, $b = 10.6948$ (10) Å, $c = 8.5994$ (13) Å, $\beta = 95.516$ (11)°, $Z = 4$) and 2-bromo-1,3,2-benzazathiaphosphole (crystal data for C_6H_5BrNPS: monoclinic, $P2_1/c$, $a = 8.5345$ (12) Å, $b = 10.6990$ (14) Å, $c = 8.8213$ (7) Å, $\beta = 94.705$ (8)°, $Z = 4$) are isostructural and adopt dimeric structures, with long P–Z bonds. Moreover, the heterocyclic units are close to planar demonstrating an inherent thermodynamic stability for the heteronaphthalenic framework. Consequently the covalent halides **2** can be considered partially ionic, intermediate between that of the ionic salts and a purely covalent system, or a weak Lewis adduct of the cation **1** and a halide.

Introduction

The second-row non-metal elements (B, C, N, O, F) are unique in their ability to form strong pπ-bonds with many elements. Sulfur is often included in this category and theoretical pπ bond strengths for atoms bound to sulfur are comparable with those of the same elements bound to nitrogen (e.g. P=N 44, P=S 40 kcal mol^{-1}).[2] In this context, we have recently reported the preparation and characterization of a number of components that contain the first examples of stable pπ-bonding between sulfur and the heavier elements of group 15.[3-7] The new systems (**1**[S_2P], **1**[S_2As], **1**[S_2Sb], and **1**[NSAs]) are derivatives of the cationic heteronaphthalenic framework **1**, and demonstrate the ability of sulfur to achieve effective pπ-overlap. The stability of such systems is reliant upon a Huckel number of π-electrons, and effective pπ-delocalization of molecular charge is illustrated by dramatic deshielding of the ^1H and ^{13}C NMR signals for the aromatic ring. This is consistent with the parent carbon derivatives (e.g. 1,3-benzodithiolium (**1**[S_2C])[8] and 1,3-benzothiazolium (**1**[NSC])[9] cations) and the nitrogen derivative (1,3,2-benzodithiazolium cation (**1**[S_2N]).[10,11] Furthermore, molecular planarity is observed in structural studies of **1**[S_2N],[10b,11] **1**[S_2P],[3,4] **1**[NSAs][7] and the diamino- derivative **1**[N_2P],[12] confirming the incorporation of the heteroatomic centers into the pπ-structure. Consequently, **1** represents a servicable synthetic template for the potential general development of pπ-bonding arrangements for the heavier non-metals. We now emphasize the versatility of this template, with the preparation and characterization of 1,3,2-benzazathiaphospholium (**1**[NSP]) tetrachloroaluminate. The new cation **1**[NSP] is a hybrid of the benzodithiaphospholium **1**[S_2P][3-6] and benzodiazaphospholium **1**[N_2P][12] systems and allows for a direct experimental comparison between P–S and P–N pπ-bonding. In addition, we compare the spectroscopic and structural features of the neutral covalent chloride **2**[NSPCl] (2-chloro-1,3,2-benzazathiaphosphole) and bromide **2**[NSPBr] (2-bromo-1,3,2-benzazathiaphosphole) systems. The heterocyclic units in these halides are structurally similar to that of the free

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[1] (a) Dalhousie University. (b) University of New Brunswick. Present address: Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27514.

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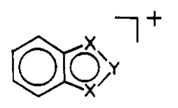
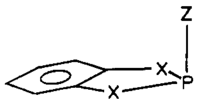
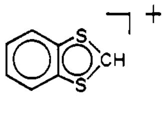
cation **1**[NSP], implying an inherent thermodynamic stability for the pπ-bonded heteronaphthalenic framework.



	X	X	Y
1[S$_2$N]:	S	S	N
1[S$_2$P]:	S	S	P
1[S$_2$As]:	S	S	As
1[S$_2$Sb]:	S	S	Sb
1[NSP]:	NH	S	P
1[NSAs]:	NH	S	As

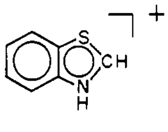


	X	X	Z
2[S$_2$PCl]:	S	S	Cl
2[S$_2$PBr]:	S	S	Br
2[NSPCl]:	NH	S	Cl
2[NSPBr]:	NH	S	Br



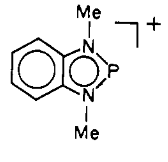
1[S$_2$C]

X = S Y = CH



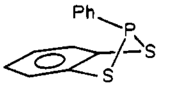
1[NSC]

X = NH X = S Y = CH



1[N$_2$P]

X = NMe Y = P



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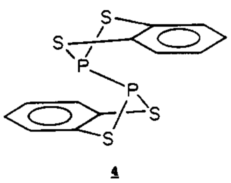

4

Experimental Section

General Procedures. *o*-Aminothiophenol and phosphorus tribromide (Aldrich) were used as received; phosphorus trichloride (Aldrich) and triethylamine (Aldrich) were distilled before use. AlCl$_3$ (Aldrich) was sublimed under vacuum and stored under nitrogen. CH$_2$Cl$_2$, CD$_2$Cl$_2$, and CDCl$_3$ were dried over P$_2$O$_5$ and stored over CaH$_2$. Diethyl ether was dried over CaH$_2$. All solvents were degassed before use. Reactions were performed in evacuated dual compartment vessels, which were flame-dried before use. Solids were handled in a nitrogen-filled drybox. IR spectra were recorded as Nujol mulls on CsI with a Perkin-Elmer 283B spectrophotometer. NMR spectra were recorded on a Nicolet NT-360 spectrometer in CDCl$_3$, CD$_2$Cl$_2$, or CH$_2$Cl$_2$. Chemical shifts are reported in ppm relative to external (85% H$_3$PO$_4$ for ^{31}P and [Al(H$_2$O)$_6$]$^{3+}$ for ^{27}Al) and internal (residual protio-CDCl$_3$ or CD$_2$Cl$_2$ for ^{1}H and CH$_2$Cl$_2$ for ^{13}C) standards. Low resolution mass spectra were obtained with a CEC Model 21-104 mass spectrometer. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratories, Gottingen, FRG.

Preparation of 2-Chloro-1,3,2-benzazathiaphosphole (2[NSPCl]). The reaction of PCl$_3$ with *o*-aminothiophenol has been alluded to by Pudovik;[13] however, experimental details were not reported. A solution of phosphorus trichloride (0.8 mL, 1.3 g, 9.4 mmol) in diethyl ether (15 mL) was added to a stirred suspension of *o*-aminothiophenol (1.0 mL, 1.2 g, 9.4 mmol) and triethylamine (2.6 mL, 1.0 g, 9.4 mmol) in diethyl ether (15 mL) over a period of 30 min, under an atmosphere of dry nitrogen. A white precipitate of triethylammonium chloride formed immediately. The reaction was stirred overnight, and the solution was then decanted. The solvent was removed from the filtrate by evacuation to leave a beige solid, which was characterized as 2-chloro-1,3,2-benzazathiaphosphole (**2**[NSPCl]): mp 83–84 °C; yield 1.5 g, 8.0 mmol, 85% (crude yield). The sample was recrystallized from CH$_2$Cl$_2$ by slow evaporation of the solvent under vacuum, and the crystals were filtered from the remainder of the solution. Anal. Calcd for C$_6$H$_5$NSPCl: C, 38.01; H, 2.66; N, 7.39. Found: C, 37.77; H, 3.14; N, 7.34. IR: 3300 (m, N–H), 1580 (m), 1370 (s), 1305 (s), 1255 (s), 1130 (m), 910 (vs), 750 (vs), 730 (m, sh), 715 (m, sh), 610 (m), 580 (s, br), 500 (vs), 485 (m), 350 (s), 290 (vs, br) cm^{-1}. Mass spectrum [*m*/*z* (relative intensity ^{35}Cl)]: 153 (100), 63 (28). NMR: ^{31}P, 160.0 (br, s); ^{1}H, 7.57–7.08 (m, 4 H, ABCDX pattern, aromatic), 6.75 (br d, 1 H, N–H, $^2J_{PH}$ = ca. 30 Hz); ^{13}C {^{1}H}, 143.2 (d, $^2J_{CP}$ = 16 Hz), 126.5, 125.0, 123.9, 122.4, 114.3. Crystals suitable for X-ray diffraction studies were obtained from a dilute diethyl ether solution by slow evaporation to produce a beige oil, which crystallized on standing under vacuum overnight.

Table I. Crystal, Data Collection, and Refinement Parameters for [**1**[NSP]]AlCl$_4$, **2**[NSPCl], and **2**[NSPBr][a]

formula	C$_6$H$_5$AlCl$_4$NPS	C$_6$H$_5$ClNPS	C$_6$H$_5$BrNPS
mol wt	322.83	189.60	234.05
a, Å	6.4773 (6)	8.5607 (10)	8.5345 (12)
b, Å	23.5434 (21)	10.6948 (10)	10.6990 (14)
c, Å	8.5101 (6)	8.5994 (13)	8.8213 (7)
β, deg	98.048 (7)	95.516 (11)	94.705 (8)
V, Å^3	1284.99	783.67	802.76
Z	4	4	4
D_{calcd}, Mg m^{-3}	1.669	1.607	1.937
μ, mm^{-1}	1.24	0.86	5.44
R_f	0.035	0.035	0.056
R_w	0.047	0.044	0.066

[a] All compounds adopt the space group $P2_1/c$. The data were collected at room temperature by using Mo Kα (λ = 0.709 30 Å) radiation.

Preparation of 2-Bromo-1,3,2-benzazathiaphosphole (2[NSPBr]). A solution of triethylamine (2.6 mL, 1.9 g, 19 mmol) in CH$_2$Cl$_2$/diethyl ether (1:1, 15 mL) was added to a solution of *o*-aminothiophenol (1.0 mL, 1.2 g, 9.4 mmol) in CH$_2$Cl$_2$/diethyl ether (1:1, 15 mL). On stirring, the yellow solution produced a pale white precipitate of triethylammonium chloride. A solution of phosphorus tribromide (0.9 mL, 2.5 g, 9.4 mmol) in CH$_2$Cl$_2$/ether (1:1, 15 mL) was added and the mixture was stirred for 3 h, at room temperature, enhancing precipitation. A pale yellow solution was decanted from the precipitate and the solvent was slowly removed by evaporation under vacuum to leave yellow crystals suitable for crystallography, which were filtered from the remainder of the solution, and characterized as 2-bromo-1,3,2-benzazathiaphosphole (**2**[NSPBr]): mp 139–142 °C; yield 1.0 g, 4.4 mmol, 47%. Anal. Calcd for C$_6$H$_5$NSPBr: C, 30.79; H, 2.16; N, 5.99. Found: C, 30.85; H, 2.38; N, 5.93. IR: 3330 (m, N–H), 1575 (m), 1470 (s), 1365 (s), 1300 (s), 1250 (m), 1020 (m), 900 (vs), 840 (m), 815 (m), 750 (vs), 620 (s), 610 (s), 500 (vs), 475 (m), 435 (m), 340 (s), 320 (m), 245 (vs) cm^{-1}. Mass spectrum [*m*/*z* (relative intensity ^{79}Br]: 153 (100), 80 (20). NMR: ^{31}P, 175.2; ^{13}C {^{1}H}, 114.8, 122.2, 125.0, 126.5 (quaternary carbons not observed due to low solubility); ^{1}H (CD$_2$Cl$_2$), 7.61–7.11 (complex multiplet ABCDX), 6.71 (br d, N–H, $^2J_{PH}$ = ca. 34 Hz).

Preparation of 1,3,2-Benzazathiaphospholium (1[NSP]) Tetrachloroaluminate. A solution of 2-chloro-1,3,2-benzazathiaphosphole **2**[NSPCl] (0.8 g, 4.1 mmol) in CH$_2$Cl$_2$ (10 mL) was poured in small portions onto a vigorously stirred suspension of AlCl$_3$ (0.6 g, 4.1 mmol) in CH$_2$Cl$_2$ (10 mL). A bright orange solution formed immediately and the reaction mixture was stirred at room temperature for 3 h. Slow evaporation of approximately 80% of solvent and cooling of the concentrated solution provided bright yellow crystals, which were filtered from the solution and characterized as 1,3,2-benzazathiaphospholium (**1**[NSP]) tetrachloroaluminate: mp 123–125 °C; yield 0.8 g, 2.2 mmol, 53%. Anal. Calcd for C$_6$H$_5$NSPAlCl$_4$: C, 22.33; H, 1.57; N, 4.34. Found: C, 22.12; H, 1.88; N, 4.33. IR: 3200 (br, m, N–H), 1580 (s), 1365 (s), 1250 (m), 1240 (s), 1175 (br, m), 920 (s), 770 (vs), 740 (m), 725 (s), 550 (s), 510 (vs, sh), 485 (vs), 445 (m, sh) cm^{-1}. Mass spectrum [*m*/*z* (relative intensity) ^{35}Cl]: 153 (100), 35 (12). NMR: ^{31}P, 306; ^{27}Al, 102 ($\Delta\nu_{1/2}$ < 15 Hz); ^{1}H, 8.34–7.89 (m, ABCDX pattern, aromatic). These peaks mask the majority of the signal assigned to the amine proton, which is centered at 8.3 ppm; ^{13}C {^{1}H}, 148.1, (d, $^2J_{CP}$ = 3.0 Hz), 135.6 (d, $^2J_{CP}$ = 3.4 Hz), 131.4, 129.0, 125.8, 118.9.

Reaction of 2[NSPBr] with AlCl$_3$. **2**[NSPBr] (0.091 g, 0.39 mmol) and AlCl$_3$ (0.052 g, 0.39 mmol) were combined in a bulb of a vacuum vessel equipped with a 10 mm o.d. NMR tube. A small amount of CH$_2$Cl$_2$ (15 mL) was distilled onto the mixture and the resulting green/yellow solution was stirred at room temperature for 1 h. An NMR study indicated the formation of **1**[NSP] in >90% yield: ^{31}P NMR, 300; ^{27}Al, 103 ($\Delta\nu_{1/2}$ < 15 Hz), 99 ($\Delta\nu_{1/2}$ < 30 Hz), 94.

X-ray Data Collections, Solutions, and Refinement. Block-shaped crystals of [**1**[NSP]]AlCl$_4$, **2**[NSPCl], and **2**[NSPBr] were obtained as described above and were selected in the drybox and mounted in Pyrex capillaries. An Enraf-Nonius CAD-4 diffractometer was used to measure the unit cell dimensions and to collect the data at room temperature (20 °C), using graphite monochromated Mo Kα radiation (λ = 0.709 30 Å). The crystal data and data collection details are listed in Table I. The unit cell constants were obtained by least-squares analysis of the dif-

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[13] Pudovick, M. A.; Mikhailov, Y. B.; Pudovick, A. N. *Zh. Obshch. Khim.* **1985**, *55*, 1475.

Table II. Final Atomic Coordinates for [**1**[NSP]]$AlCl_4$

	x	y	z	B_{iso},[a] Å^2
Al(1)	0.96895 (14)	0.65179 (4)	0.24511 (11)	0.340 (4)
Cl(1)	1.07789 (15)	0.72360 (4)	0.12700 (11)	5.02 (4)
Cl(2)	1.16052 (15)	0.63390 (4)	0.46082 (11)	5.07 (4)
Cl(3)	0.65609 (13)	0.66661 (4)	0.28549 (12)	4.99 (4)
Cl(4)	0.97440 (16)	0.58173 (4)	0.08541 (10)	4.96 (4)
S(1)	0.33595 (15)	0.31672 (4)	0.25438 (12)	4.89 (4)
P(1)	0.55753 (17)	0.29427 (4)	0.11873 (12)	4.85 (5)
N(1)	0.6452 (4)	0.35943 (12)	0.1082 (3)	4.28 (13)
C(1)	0.5549 (5)	0.40425 (14)	0.1796 (3)	3.86 (13)
C(2)	0.6177 (6)	0.46082 (15)	0.1749 (4)	4.97 (17)
C(3)	0.5102 (8)	0.50046 (16)	0.2484 (5)	6.14 (22)
C(4)	0.3438 (7)	0.48485 (17)	0.3274 (4)	5.91 (21)
C(5)	0.2841 (6)	0.42982 (18)	0.3359 (4)	5.14 (17)
C(6)	0.3907 (5)	0.38875 (14)	0.2605 (4)	3.95 (14)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table III. Final Atomic Coordinates for **2**[NSPCl]

	x	y	z	B_{iso},[a] Å^2
S(1)	0.42258 (6)	0.37435 (5)	0.24290 (6)	3.420 (21)
P(1)	0.46443 (6)	0.56541 (5)	0.27334 (6)	3.309 (21)
Cl(1)	0.28983 (7)	0.60881 (6)	0.44442 (6)	4.316 (24)
N(1)	0.36705 (22)	0.60103 (6)	0.10350 (20)	3.42 (7)
C(1)	0.27066 (22)	0.51269 (20)	0.02121 (22)	3.11 (8)
C(2)	0.1717 (3)	0.53950 (25)	−0.1115 (3)	4.09 (10)
C(3)	0.0848 (3)	0.4426 (3)	−0.1836 (3)	4.77 (12)
C(4)	0.0955 (3)	0.3232 (3)	−0.1239 (3)	4.90 (12)
C(5)	0.1959 (3)	0.29539 (23)	0.0078 (3)	4.13 (9)
C(6)	0.28308 (24)	0.39236 (19)	0.07953 (23)	3.09 (8)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table IV. Final Atomic Coordinates for **2**[NSPBr]

	x	y	z	B_{iso},[a] Å^2
Br(1)	0.72054 (8)	0.10476 (6)	0.04049 (7)	4.03 (3)
P(1)	0.53304 (18)	0.05788 (13)	0.23436 (17)	3.15 (6)
S(1)	0.57453 (19)	−0.13256 (13)	0.26426 (17)	3.36 (6)
N(1)	0.6345 (6)	0.0943 (4)	0.3968 (6)	3.25 (20)
C(1)	0.7301 (7)	0.0056 (6)	0.4757 (6)	3.20 (23)
C(2)	0.8291 (8)	0.0317 (6)	0.6050 (7)	4.0 (3)
C(3)	0.9134 (8)	−0.0655 (9)	0.6747 (8)	5.2 (4)
C(4)	0.9006 (8)	−0.1861 (8)	0.6185 (8)	4.9 (3)
C(5)	0.8009 (8)	−0.2133 (6)	0.4898 (8)	4.3 (3)
C(6)	0.7150 (7)	−0.1166 (5)	0.4205 (7)	3.07 (22)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

fractometer setting angles of 25 well-centered reflections. A $\theta/2\theta$ scan mode was employed with $2\theta_{max}$ of 49.9°. The intensities of three standard reflections were monitored and showed no significant variation in intensity during the data collection. The space group was determined to be $P2_1/c$ (monoclinic) for all three compounds, by the systematic absences.

Scattering factors for neutral atoms were corrected for anomalous dispersion.[14] The structures were solved by direct methods and refined by a full matrix least-squares procedure[15] using anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atom positions were located from a difference-Fourier map and included in the final cycles of refinement with the isotropic thermal parameter of the atom to which they are attached. The function minimized was $\Sigma w(\Delta F_o)^2$, where $w = 1/(\sigma^2(F_o) + 0.00005(F_o)^2)$ and σ was obtained from counter statistics. No corrections were applied for absorption or extinction. All calculations were performed by NRCVAX.[15] Final atomic coordinates are provided in Tables II–IV, and selected bond lengths and angles for the heterocyclic units of [**1**[NSP]]$AlCl_4$, **2**[NSPCl], and **2**[NSPBr] are listed in Table V and are compared with those for **1**[S_2P], **1**[N_2P], and **3**. Long intermolecular contacts are presented in Table VI.

Results and Discussion

Synthesis and Spectroscopic Characterization. *o*-Aminothiophenol reacts with PCl_3 and PBr_3 in the presence of triethylamine to give the corresponding derivatives of the 1,3,2-benzazathiaphosphole framework, **2**[NSPCl] and **2**[NSPBr], respectively, in reasonable yield. This metathetical cyclization procedure has some synthetic versatility for organo-non-metal five-membered ring formation;[3-5,7,10,12,13,16] however, we have been unable to obtain satisfactory results with *o*-phenylenediamine.

Both halides react rapidly with $AlCl_3$ in CH_2Cl_2 to give the cationic species **1**[NSP] in good yield. The formation of the tetrahaloaluminate anions is evidenced by the characteristic signals in the ^{27}Al NMR spectra.[7,17] A sharp signal at 103 ppm ($\Delta\nu_{1/2} < 15$ Hz) is observed for [**1**[NSP]]$AlCl_4$. The same signal is observed in the reaction mixture of **2**[NSPBr] with $AlCl_3$, together with broader signals at 99 and 94 ppm, which we assign to $AlCl_3Br^-$ and $AlCl_2Br_2^-$, respectively.[18] Although, we do not observe $AlClBr_3^-$ or $AlBr_4^-$, formation of the mixed anions is consistent with previous studies on tetrahaloaluminate anions in CH_2Cl_2.[19] In the solid state, the strong band at 485 cm^{-1} in the infrared spectrum of **1**[NSP]$AlCl_4$ is characteristic for the $AlCl_4^-$ anion,[20] and is absent in the spectra of **2**[NSPCl] and **2**[NSPBr]. The N–H stretch is observed in all spectra. Otherwise, the IR spectra exhibit very similar features to those for other derivatives of **1** and **2**.[4-6] The mass spectra of **2**[NSPCl] and **2**[NSPBr] show a very small molecular ion peak. The base peak corresponds to an elimination (of HCl and HBr, respectively) product. By comparison, compound **2**[S_2PCl] shows loss of chlorine; however, the molecular ion is more pronounced. In common with many non-metal salt systems (including [**1**[S_2P]]$AlCl_4$),[4] [**1**[NSP]]$AlCl_4$ shows a mass spectrum identical with that of **2**[NSPCl], suggesting the formation of **2**[NSPCl] in the mass spectrometer source.[21]

While ^{31}P NMR chemical shifts are influenced by a number of factors,[22] the relative electronegativity of Z is apparently the most important for derivatives of **2** ([S_2PCl] 157,[23a] 161;[23b] [S_2PBr] 165;[23b] [NSPCl] 160; [NSPBr] 175 ppm) and **3** (50 ppm).[16a] The shifts of the chlorine derivatives (**2**[NSPCl] and **2**[S_2PCl]) are very similar, while the bromides (**2**[NSPBr] and **2**[S_2PBr]) are slightly deshielded and the phenyl derivative (**3**) has the most shielded phosphorus center. The ^{31}P signals of the corresponding cations are dramatically deshielded from those of the neutral halides, confirming the cationic nature in solution. The chemical shift trend, **1**[S_2P] (408) < **1**[NSP] (306)[24] < **1**[N_2P] (212), is a reflection of the combined effects of the relative σ-withdrawal and π-donor strengths of nitrogen and sulfur and the degree of π-delocalization of molecular charge (the selenium derivative of **1**, 1,3,2-benzodiselenaphospholium, exhibits a downfield ^{31}P signal at 495 ppm).[25] In addition we note that the n–π^* energy separation follows a similar trend [**1**[S_2P] < **1**[NSP] < **1**[N_2P]] (vide infra), which has a significant influence on the paramagnetic shielding contribution at phosphorus.[26] The

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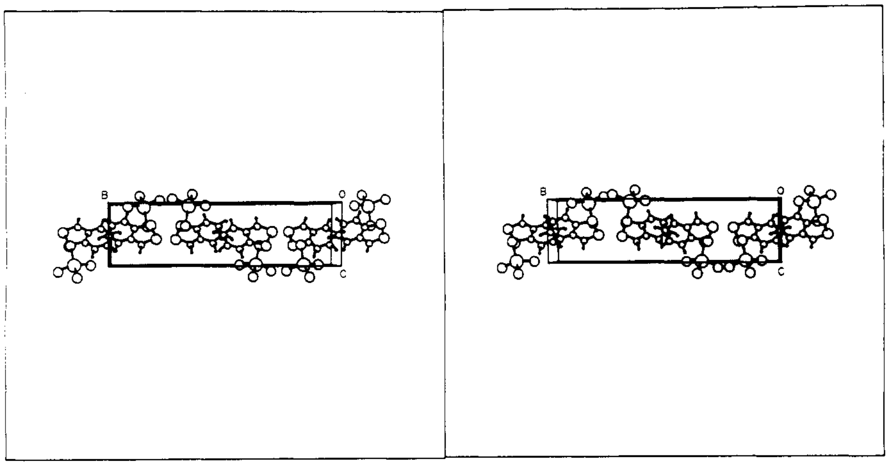

Figure 1. Stereoview of the unit cell of [**1**[NSP]]$AlCl_4$.

Table V. Selected Bond Distances (Å) and Angles (deg) for **1**[NSP], **2**[NSPCl], and **2**[NSPBr], and a Comparison of Pertinent Values for Cations **1**[S_2P] and **1**[N_2P] and the Neutral System **3**

	1[S_2P][a]	**1**[N_2P][b]	**1**[NSP]	**2**[NSPCl]	**2**[NSPBr]	**3**[a]
S(1)–P(1)	2.016 (3) 2.015 (3)		2.0337 (14)	2.0886 (9)	2.081 (2)	2.110 (2) 2.102 (2)
N(1)–P(1)		1.643 (6)	1.643 (3)	1.655 (2)	1.659 (5)	
N(1)–C(1)		1.379 (9)	1.387 (4)	1.401 (3)	1.399 (8)	
S(1)–C(6)	1.728 (5) 1.711 (6)		1.732 (4)	1.765 (2)	1.759 (6)	1.761 (5) 1.765 (6)
P(1)–Z(1)				2.2443 (9)	2.487 (2)	1.827 (4)
C(1)–C(6)	1.383 (7)	1.378 (10)	1.394 (5)	1.382 (3)	1.398 (8)	1.401 (6)
C(1)–C(2)	1.411 (8)	1.403 (10)	1.395 (5)	1.384 (3)	1.391 (8)	1.389 (7)
C(2)–C(3)	1.350 (10)	1.379 (11)	1.367 (6)	1.387 (4)	1.380 (11)	1.377 (8)
C(3)–C(4)	1.351 (10)	1.390 (12)	1.397 (7)	1.375 (4)	1.384 (13)	1.386 (7)
C(4)–C(5)	1.374 (9)	1.366 (11)	1.357 (6)	1.389 (4)	1.393 (10)	1.378 (8)
C(5)–C(6)	1.407 (8)	1.408 (11)	1.395 (5)	1.387 (3)	1.381 (8)	1.377 (8)
S(1)–P(1)–E	97.59 (10) (S–P–S)	91.3 (3) (N–P–N)	93.74 (11) (S–P–N)	92.80 (7) (S–P–N)	92.8 (2) (S–P–N)	94.9 (1) (S–P–S)
C(1)–N(1)–P(1)		114.2 (5)	121.1 (2)	120.85 (14)	120.8 (4)	
C(6)–S(1)–P(1)	102.6 (2) 102.5 (2)		96.54 (12)	95.04 (7)	95.9 (2)	99.1 (2) 99.6 (2)
S(1)–P(1)–Z(1)				99.65 (3)	99.91 (7)	101.0 (2) 104.5 (2)
N(1)–P(1)–Z(1)				102.72 (7)	103.1 (2)	
N(1)–C(1)–C(6)		110.1 (6)	114.5 (3)	115.1 (2)	115.4 (5)	
S(1)–C(6)–C(1)	120.2 (4) 121.4 (4)		114.1 (3)	114.41 (15)	113.6 (4)	118.8 (4) 118.8 (4)
C(6)–C(1)–C(2)	119.1 (5)	121.0 (7)	120.6 (3)	120.8 (2)	120.4 (6)	120.0 (5)
C(1)–C(2)–C(3)	118.0 (6)	117.3 (7)	118.0 (3)	118.2 (3)	118.3 (6)	120.8 (4)
C(2)–C(3)–C(4)	122.6 (6)	121.3 (7)	121.1 (4)	120.9 (2)	121.3 (6)	118.4 (5)
C(3)–C(4)–C(5)	122.39 (6)	122.0 (7)	121.4 (4)	121.2 (2)	120.8 (6)	121.8 (6)
C(4)–C(5)–C(6)	116.0 (6)	117.2 (7)	118.3 (4)	117.9 (2)	118.1 (7)	119.8 (5)
C(5)–C(6)–C(1)	122.1 (5)	121.2 (7)	120.4 (3)	121.0 (2)	121.1 (6)	119.3 (5)

[a] References 3 and 4. Atomic numbering has been changed to allow easy comparison. [b] Reference 12.

Table VI. Distances (Å) and Angles (deg) of Long Intermolecular Contacts in [**1**[NSP]]$AlCl_4$, **2**[NSPCl], and **2**[NSPBr] (within the Sum of the van der Waals Radii)

[**1**[NSP]]$AlCl_4$			**2**[NSPCl]	**2**[NSPBr]
P–Cl(1)l	3.405 (2)	P–Z′	3.5786 (9)	3.568 (2)
P–Cl(1)b	3.393 (1)	Z–Z′	4.315 (1)	4.389 (1)
		P–P′	4.132 (1)	4.309 (3)
P–Cl(3)e	3.642 (2)	P–S′	3.4493 (8)	3.437 (2)
P–Cl(3)k	3.454 (1)	S–Z′	3.4715 (9)	3.542 (2)
		N–Z′	3.430 (2)	3.516 (4)
S–Cl(3)k	3.551 (1)			
S–Cl(1)k	3.711 (1)	P–Z–P′	87.24 (3)	88.87 (5)
		Z–P–Z′	92.76 (3)	91.13 (5)
N–Cl(1)b	3.471 (3)			
N–Cl(4)b	3.441 (3)			

downfield shift of the ^1H and ^{13}C NMR signals for **1**[NSP], with respect to those of **2**[NSPCl] and **2**[NSPBr] demonstrates charge delocalization into the benzo moiety, consistent with other derivatives of **1**.[4,5,8,9]

Crystal and Molecular Structure of 1,3,2-Benzazathiaphospholium (1[NSP]) Tetrachloroaluminate. The structure consists of discrete cationic and anionic units with long distance contacts between the chlorine atoms of the anion and the sulfur, phosphorus, and nitrogen centers of the cation. A stereoview of the unit cell is shown in Figure 1[27] and a view of the cation is presented in Figure 2[28] (bond lengths and angles, Table V), showing the cation/anion contacts (see also Table VI), which are within the sum of the van der Waal's radii for the atoms involved (P, 1.9 Å; Cl, 1.80 Å).[29] Two of these contacts are localized at the phosphorus center above and below the heterocyclic plane. Of the four in-plane cation/anion interactions, two bridge the P–S

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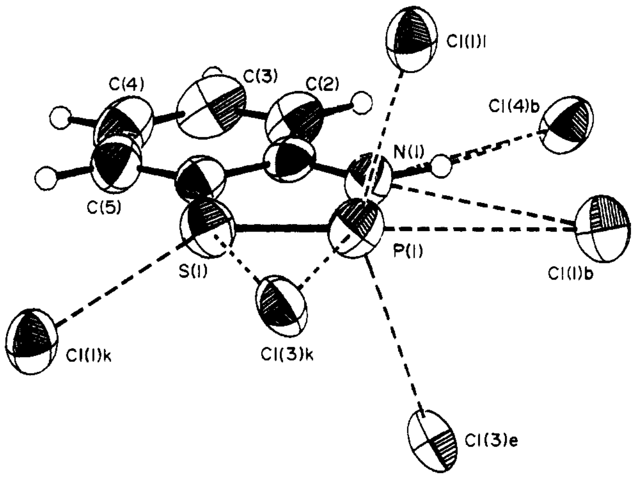

Figure 2. ORTEP view of cation **1**[NSP] showing the cation/anion contacts which are within the sum of the van der Waals' radii.

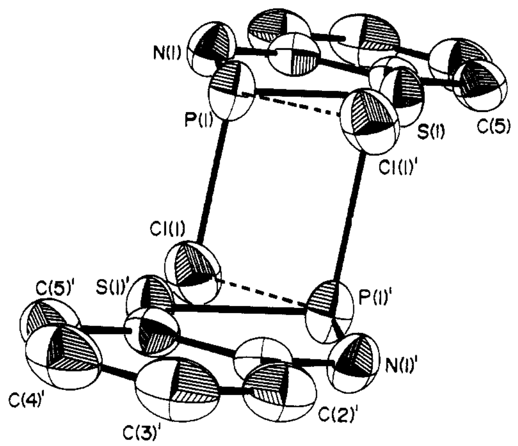

Figure 3. Representative view of the dimeric unit for **2**[NSPCl]. Dotted lines indicate long contacts; see Table VI.

and P–N bonds, while the others are localized at the sulfur and nitrogen centers, respectively. The latter is also an H···Cl interaction and can be viewed as a weak hydrogen bond.[30] Nevertheless, the array of contacts is very similar to that observed for other derivatives of $\mathbf{1}AlCl_4$.[4,7,12] In fact, the tetrachloroaluminate salts of $\mathbf{1}[S_2P]$,[4] **1**[NSP], and **1**[NSAs][7] are isostructural, demonstrating the isolobal relationship between a dicoordinate NH unit and a dicoordinate sulfur center.[31]

Similar contacts have been observed for other hetero- and homopolyatomic main group cations,[32] such as Ch_4^{2+} (Ch = S, Se, Te) or Se_8^{2+} and have been interpreted as donations from the anion to the electrophilic centers of the cation.[33] The isostructural nature of the $AlCl_4^-$ salts of $\mathbf{1}[S_2P]$, **1**[NSP], and **1**[NSAs] implies that the intermolecular interactions play an important role in crystal packing. However, these interactions are weaker than other $AlCl_4^-$ salts (e.g. chlorotin(II) cations[34,35]), where the tetrachloroaluminate anion shows significant distortion.

Cation **1**[NSP] is planar with a maximum deviation from the plane of 0.045 (5) Å at C(4). All derivatives of **1** exhibit short bond lengths within the heterocyclic framework. While the P–S bond length (2.0337 (14) Å) in **1**[NSP] is slightly longer than that in $\mathbf{1}[S_2P]$ (2.016 (3), 2.015 (3) Å),[3,4] it is significantly shorter than that of a typical P(III)–S σ-bond (for example, P_4S_3, 2.09 Å[36] and $(PhS)_3P$, 2.112 (1) Å).[37] Similarly, the P–N bond (1.643 (3) Å) in **1**[NSP] is comparable to that of other cationic diaminophosphorus centers (e.g. 1.611 (4) Å in $[(i\text{-}Pr)_2N]P^+$,[38] 1.633 (3) Å in $Me_2Si(NtBu)_2P^+$ [39]) and is identical with that in the corresponding 1,3,2-benzodiazaphospholium cation $\mathbf{1}[N_2P]$[12] (1.643 (6) Å). The C–S bond (1.732 (4) Å; cf. 1.802 (2) Å in Me_2S)[40] and the C–N bond (1.387 (4) Å; cf. 1.474 Å in NH_2CH_3)[36] are also short and are identical with those in $\mathbf{1}[S_2P]$ and $\mathbf{1}[N_2P]$, respectively.

Crystal and Molecular Structures of 2[NSPCl] and 2[NSPBr]. Compounds **2**[NSPCl] and **2**[NSPBr] are isostructural and consist of dimeric units of **2** (a representative view of the dimer, **2**-[NSPCl], is shown in Figure 3).[28] The monomers are related by a crystallographic inversion center and are bound together by a bridging P_2Z_2 (Z = Cl, Br) four-membered ring, which has unequal phosphorus halogen bond lengths. The shorter P–Cl (2.2443 (9) Å) and P–Br (2.487 (2) Å) distances are significantly longer than regular P–Z covalent bonds (e.g. 2.124 (3) Å, 2.020 (3) Å in PCl_5; 2.15 (3) Å in PBr_4^+ [in PBr_5]).[41] Also of interest are the long P–Z interactions (dotted bonds in Figure 3, P–Cl, 3.5786 (9) Å; P–Br, 3.568 (2) Å), which are within the sums of the van der Waals radii (P···Cl, 3.7 Å; P···Br, 3.85 Å).[29] Within each dimer, the heterocycles are essentially coplanar and perpendicular to the P_2Z_2 bridge (Figure 3).[28] However, the bridging four-membered P_2Z_2 unit is in the plane of the P–N bond, on the sulfur side of the molecule, allowing contacts between halogen and sulfur centers (S···Cl, 3.4715 (9) Å; S···Br, 3.542 (2) Å), which are slightly shorter than the long P···Z′ contacts (P···Cl, 3.5786 (9) Å; P···Br, 3.568 (2) Å) but similar to one of the principal cation/anion contacts observed in the salt of **1**[NSP].

Halogen bridged dimerization has been observed for the anions of $[N(i\text{-}Pr)_4][PBr_4]$, which adopt bond lengths similar (2.527 (4) and 3.460 (4) Å)[42] to those observed for **2**[NSPBr]. Similar arrangements are reported for $P(CN)_3Br^-$ [equivalent P–Br bond lengths (3.058 (1) Å],[42] $MeSi(NtBu)_2AsCl$,[45] and chlorotin(II) cations.[34,35] Interestingly, the anions of $[NEt_4][PBr_4]$ have a monomeric structure,[43] as do other halophosphate anions, including PCl_4^-.[44]

A contact between the aza hydrogen atom of one dimer unit and the halogen center of another represents the only lattice interaction between dimers. The heterobicyclic moieties of **2**-[NSPCl] and **2**[NSPBr] are structurally indistinguishable. As illustrated in Figure 3, the heterocycles are close to planar (maximum deviation occurs at N in both structures: **2**[NSPCl], 0.198 (2) Å; **2**[NSPBr], 0.173 (6) Å) and are structurally very similar to that of the free cation **1**[NSP]. The P–N and C–N bond lengths are identical, as are the endocyclic angles and the general structure of the benzo moiety (Table V). The P–S bonds in **2**[NSPCl] (2.0886 (9) Å) and **2**[NSPBr] (2.081 (2) Å) are longer than that of **1**[NSP] (2.0337 (14) Å) but are significantly shorter than standard P–S σ-bonds (e.g. 2.112 (1) Å)[37] and those

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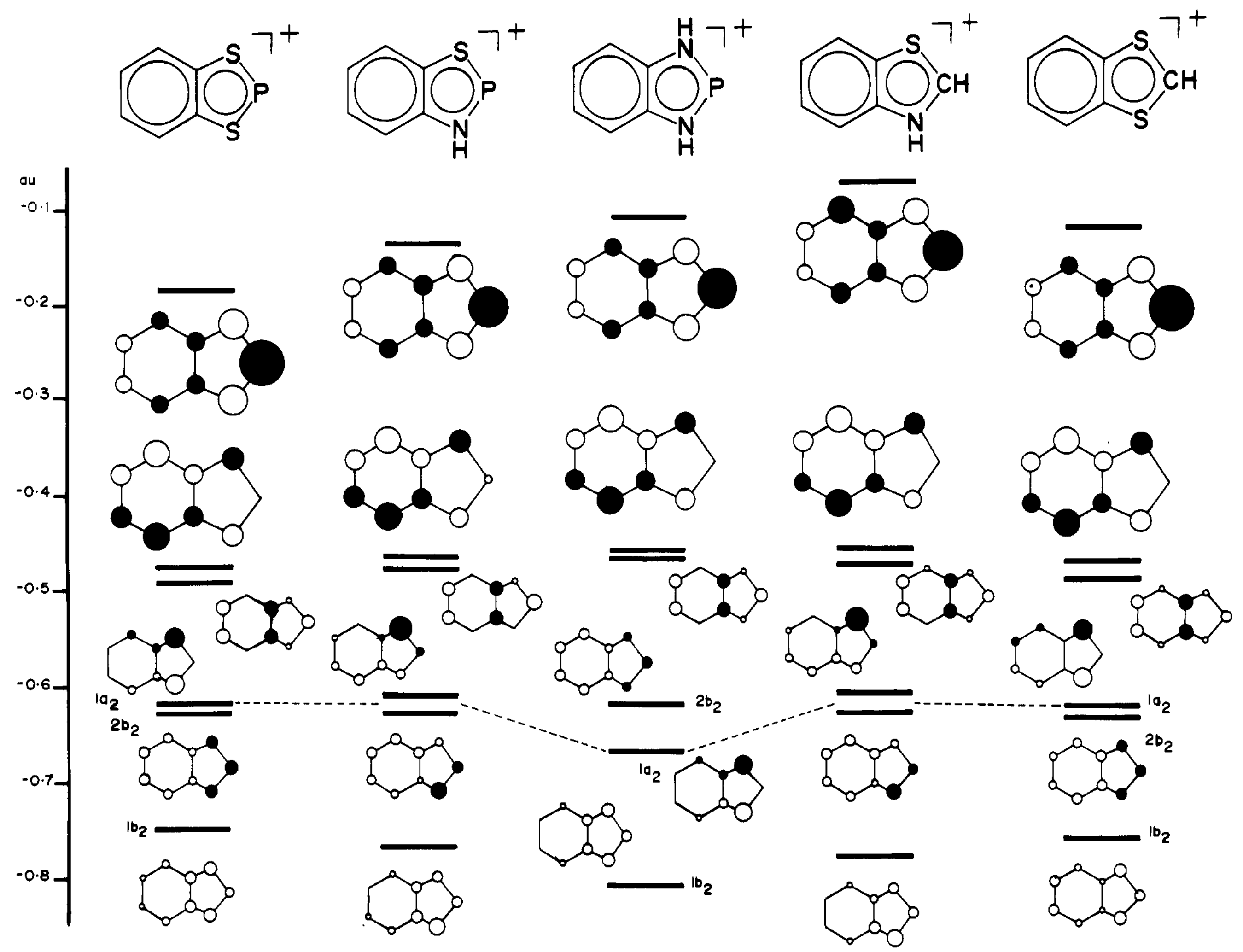

Figure 4. Energy levels for π-molecular orbitals of **1**[S_2P], **1**[NSP], **1**[N_2P], **1**[NSC], and **1**[S_2C]. Molecular orbitals are viewed from above, and size of the circles represents the eigenvector coefficient.

of the organic derivative 5-methyl-2-phenyl-1,3,2-benzodithiaphosphole (**3**) (2.110 (2) and 2.102 (2) Å).[3,4] The planarity of the heterocyclic units of **2**[NSPCl] and **2**[NSPBr] (phosphorus centers displaced from the C_6H_4NS plane by only 0.259 (2) and 0.228 (4) Å, respectively) is intermediate between that observed for the neutral phenyl derivative **3** (phosphorus center is displaced by 0.53 Å from the C_6S_2 plane),[3,4] and the planar cations **1**.

P–S and P–N π-Bonding of Comparable Energy. The spectroscopic and structural features of **1**[NSP] are consistent with a heteronaphthalenic system and a hybrid of **1**[S_2P][4] and **1**[N_2P].[12] In this context, **1**[NSP] is a rare example of a system containing thermodynamically stable pπ-bonding between phosphorus and sulfur. Although a number of factors are responsible for the overall stability of these systems, the observation of delocalized N–P–S pπ-bonding in **1**[NSP] is significant. A thermodynamic preference for P–N π-bonding would localize π-bonding in the P–N region, rendering a neutral dicoordinate sulfur center, and promote ammonium character at the nitrogen center. Consequently, cation **1**[NSP] and the series **1**[S_2P], **1**[NSP], **1**[N_2P] demonstrate energetic competition between P–S and P–N pπ-bonding (comparable pπ-bond energies for P–S and P–N) and provide experimental support for the theoretical realization that sulfur and other heavier non-metals are capable of effective, general pπ-overlap. Recent work by Power has demonstrated that shortening of bonds to phosphorus may be due to rehybridization as well as pπ-bonding.[46] However, we believe that much of the shortening of the P–S and P–N bonds, and the other heterocyclic bonds in the derivatives of **1**, is attributable to effective pπ-bonding throughout the system.

As the heteronaphthalenic nature of **1** is principally responsible for the stability of these systems, we have obtained a preliminary theoretical model by using single geometry STO-3G (GAMESS)[47] molecular orbital calculations on **1**[S_2P], **1**[NSP], and **1**[N_2P] (NH derivatives), using experimentally observed structural parameters. For direct comparison the organic derivatives 1,3-benzodithiolium **1**[S_2C] and 1,3-benzothiazolium **1**[NSC] have also been examined. The results agree well with those obtained for **1**[S_2P] and **1**[NSP] by using the π-electron Pariser, Parr, Pople calculations[48] and confirm the 10π-electron Hückel nature of these systems. Figure 4 is a graphical representation of the π-manifolds of these systems. The molecular asymmetry of **1**[NSP] and **1**[NSC] is evident in certain molecular orbitals. For example, **1**[NSP] and **1**[NSC] contain hybrids of the $1a_2$ and $2b_2$ orbitals of the symmetric systems. The higher electronegativity of nitrogen over sulfur renders the reverse ordering for these two orbitals in the diamino system **1**[N_2P]. Nevertheless, this has only a minor effect on the orbital energies and the occupied π-manifold remains remarkably constant upon substitution of the framework atoms of the heterocycle. As expected, all of the π-structures have a close resemblance to that of the indenyl anion[49] and exhibit the fundamental features of naphthalene. Recent studies on the

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1,3-benzodithiazolium cation **1**[S_2N] also show similar results.[11]

For the phosphorus cations, the calculated HOMO-LUMO and n-π^* separations are largest for **1**[N_2P] and smallest for **1**[S_2P]. While transition energies obtained in this manner are unreliable, on a comparative basis the trend is consistent with the atomic orbital energies of nitrogen and sulfur, the colors of these compounds (**1**[N_2P], colorless; **1**[NSP], pale yellow; **1**[S_2P], yellow-orange), and the UV-visible and MCD spectra of **1**[S_2P] and **1**[NSP].[48] Deviations from naphthalenic character are more prominent in the unoccupied orbitals. Of particular interest are the π-LUMOs, which are essentially identical in form throughout the series and are based primarily at the 2 position (P or CH). Therefore, in contrast to the nitrogen derivative **1**[S_2N],[11] which demonstrates an essentially equal contribution from the sulfur and nitrogen centers in the π-LUMO, nucleophilic attack is expected to predominate at the phosphorus centers of **1**[S_2P], **1**[NSP], and **1**[N_2P]. In addition, the diphosphine **4**, prepared by Baudler from the reaction of **2**[S_2PCl] with sodium,[23a] will be principally P-P σ-bonded, in contrast to the novel π^*-π^* geometry of the nitrogen derivative.[11,50,51]

Anion Basicity and Cation Stability. The identification of the cationic heteronaphthalenic framework **1** as a synthetic template was reliant upon the versatility of the halide abstraction[52] procedure for the preparation of non-metal and organic cations. For systems containing the heavier elements, the stability of the ionic arrangement over an alternative covalent arrangement is dependent upon the low basicity of the anion.[51,53] In contrast, the nitrogen derivative **1**[S_2N] is a stable ionic system as a halide salt.[10,11] The preference for π-bonding between nitrogen and sulfur precludes the formation of a weak N-Cl covalent bond, while the preference for σ-bonding for the heavier elements requires some competition for the chloride ion, by a Lewis acid, in order to stabilize the π-bonded arrangement. Nevertheless, the cations **1** require the inherent stability to avoid other possible disproportionation reactions. The covalent halides **2**[NSPCl] and **2**[NSPBr] exhibit a substantial degree of ionic character in the solid state without the presence of a Lewis acid. On this basis, we may view the derivatives of **1**, **2**, and **3** as a series of Lewis adducts of varying strength.

(1) Compound **3** contains a standard P-C covalent bond and represents the most strongly bound adduct of **1**, with Ph^- as the base (pK_a(benzene) = 43).[54]

(2) The monomeric units of the halide derivatives of **2** have partial ionic character and may be considered as ion-pairs (pK_a(HCl) = -6; pK_a(HBr) = -8).[55] The shorter P-Z covalent bond may be considered as a donation from the halide into the phosphorus-based π-LUMO of the cation from above the plane.

(3) The weakest interactions are observed in the solid-state structures of $AlCl_4^-$ salts of **1**. The long anion/cation contacts (>3.30 Å) are best envisaged as donor/acceptor interactions from the complex anion to the cation. While a number of these contacts take place at the phosphorus center above and below the plane (into π-LUMO), there are numerous in-plane interactions and contacts to the heteroatoms. Also in this category are the long intermonomer contacts observed for **2**[NSPCl] and **2**[NSPBr].

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Supplementary Material Available: Tables of crystal data, hydrogen atom coordinates, anisotropic thermal parameters, geometries for molecular orbital calculations, and calculated energies and a unit cell diagram (7 pages); tables of calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

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Contribution from the Institut für Physikalische und Theoretische Chemie, University of Erlangen-Nürnberg, D-8520 Erlangen, West Germany, Institut für Heisse Chemie, Kernforschungszentrum Karlsruhe, D-7500 Karlsruhe, West Germany, and Department of Chemistry, The University of New South Wales, Kensington, NSW 2033, Australia

Detailed Hysteresis Studies and Nature of the Spin-State Transition in Bis(1,10-phenanthroline-2-carbaldehyde phenylhydrazone)iron(II) Complexes

E. König,*[1] B. Kanellakopulos,[2] B. Powietzka,[2] and H. A. Goodwin[3]

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An extensive series of scanning curves within the hysteresis loop associated with the spin-state transition in $[Fe(phy)_2](ClO_4)_2$ has been constructed on the basis of magnetic susceptibility measurements (phy = 1,10-phenanthroline-2-carbaldehyde phenylhydrazone). The areas of scanning curves F depend on the temperature width of the curves ΔT and the value of the square of the effective magnetic moment μ_{eff}^2 defined at the center of gravity of the curves. For each value of ΔT, an approximately parabolic relation between log (F/F_{tot}) and log μ_{eff}^2 is found where F_{tot} is the area of the associated hysteresis loop. Similar results have been obtained for the spin-state-transition compound $[Fe(phy)_2](BF_4)_2$. The results for the inner scanning curves do not conform to theorem 4 of the domain theory of Everett. Symmetry relations derived on the basis of simple nucleation (VWBD) theory are not followed. The consequences of these findings are discussed. A linear relation between log (F_{max}/F_{tot}) and the reduced width $\Delta T/\Delta T_{tot}$ has been empirically established where F_{max} is the maximum area of the scanning curves for a particular value of ΔT. The relation has been verified for the right boundary scanning curves of $[Fe(phy)_2]X_2$, X = ClO_4 and BF_4, and $[Fe(bpp)_2](BF_4)_2$ (bpp = 2,6-bis(pyrazol-3-yl)pyridine).

Spin-state transitions in complexes of certain transition-metal ions often proceed as phase transitions of first order.[4] Evidence for the thermodynamic character of the transition is provided by the discontinuous change of entropy (following from calorimetric[5] and DSC measurements[6-8]) and volume (derived from X-ray

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(1) University of Erlangen-Nürnberg.

(2) Kernforschungszentrum Karlsruhe.

(3) The University of New South Wales.

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