geneous-valence Rh_2^{4+} dimer whereas complexes **2** and **3** are best described as mixed-valence complexes with nonintegral oxidation states.

Acknowledgment. We thank Dr. B. E. Mann (University of Sheffield) for the ^{103}Rh NMR spectra and the Public Ministry of Education for financial support.

Registry No. **1**, 117369-58-1; **2**, 117340-66-6; **3**, 117340-67-7; $Rh_2(form)_3(NO_3)_2$, 99416-57-6; Rh, 7440-16-6.

Supplementary Material Available: Tables SI-SVI, listing atomic distances and angles associated with the tolyl, phenyl, and nitrate groups, hydrogen atom parameters, and temperature factors (10 pages); tables of calculated and observed structure factors (32 pages). Ordering information is given on any current masthead page.

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pπ-pπ Bonding between Phosphorus and Sulfur: Synthesis and Characterization of a Dithiaphospholium Cation[1]

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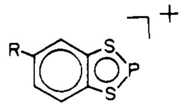
Received May 20, 1988

Salts of the first dithiaphospholium cation have been isolated and fully characterized as aromatic derivatives. The synthesis involves a chloride ion abstraction in CH_2Cl_2. The competitive aromatic electrophilic substitution is avoided by the use of high dilution conditions. An X-ray crystal structure of 1,3,2-benzodithiaphospholium (**1a**) tetrachloroaluminate indicates a planar geometry for the cation with short P-S bonds (mean 2.016 (2) Å) and short C-S bonds (mean 1.719 (4) Å). Crystal data for $C_6H_4S_2PAlCl_4$: monoclinic, space group $P2_1/c$, $a = 6.605$ (3) Å, $b = 23.377$ (4) Å, $c = 8.666$ (2) Å, $\beta = 100.28$ (3)°, $V = 1316.5$ Å^3, $Z = 4$, $R = 0.036$. The spectroscopic and structural data are interpreted in terms of unique 3pπ-3pπ bonding across the S-P-S moiety. This is highlighted by the crystal structure of the P-S σ-bonded 5-methyl-2-phenyl-1,3,2-benzodithiaphosphole (**2c**), which has P-S bonds of 2.110 (2) and 2.102 (2) Å. Crystal data for $C_{13}H_{11}S_2P$: monoclinic, space group $P2_1/n$, $a = 14.691$ (3) Å, $b = 6.291$ (1) Å, $c = 14.882$ (3) Å, $\beta = 114.56$ (2)°, $V = 1250.9$ Å^3, $Z = 4$, $R = 0.037$. The new cation contains the first example of thermodynamically stable pπ-pπ bonding between phosphorus and sulfur and, in addition, a rare example of pπ-pπ bonding between the heavier elements of different groups of the periodic table. The stabilizing features of charge and aromatic π-electron count offer great generality and indicate the potential for the formation of an extensive series of compounds containing pπ-pπ bonding between the heavier non-metal elements.

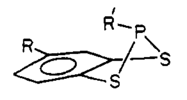
Introduction

The π-bond is often the origin of diverse and exciting chemistry. However, very few elements are observed to employ general stable pπ-bonding.[3] Kutzelnigg has suggested that weak pπ-bonding is standard for the non-metals and that the very strong pπ-bonds observed for carbon, nitrogen, and oxygen are anomalous.[4] Nevertheless, examples of compounds containing stable pπ-bonding between the heavier non-metal elements have been prepared and fully characterized. On this basis, Schmidt and Gordon have predicted that "Eventually compounds representing all possible double bonds between atoms of groups 14-16 will be isolated and characterized", and have provided useful theoretical π-bond strengths between many non-metal elements.[5]

Despite the thermodynamic preference for σ-bonding over π-bonding exhibited by most non-metal elements, specific structural or electronic features have been used to stabilize systems employing (np-np)π bonding, where $n > 2$. However, the imposition of these features is restricted and is dependent upon the fundamental periodic chemical properties of the elements involved. For example, pπ-bonds between the heavier elements of groups 14 and 15 can be kinetically stabilized by the steric constraints of bulky substituent groups.[6] Such arrangements are not possible for elements of groups 16 and 17 due to the greater number of valence electrons. Instead, pπ-bonding between the chalcogens and halogens can be induced by the presence of a molecular positive charge,[7,8] a feature that has not yet been exploited for the elements of groups 14 and 15. Consequently, experimental evidence for pπ-pπ bonding between the heavier elements ($n > 2$) from opposite sides of the p-block is not available. In an attempt to develop more general non-metal pπ-bonding, we describe the synthesis and spectroscopic characterization of the first dithiaphospholium cation, which contains a unique example of thermodynamically stable 3pπ-3pπ bonding between phosphorus and sulfur. The crystal structure of 1,3,2-benzodithiaphospholium (**1a**) tetrachloroaluminate is presented as supportive evidence for a delocalized pπ-structure. A direct comparison with a fully σ-bonded system is discussed on the basis of the crystal structure of the derivative parent phosphine, 5-methyl-2-phenyl-1,3,2-benzodithiaphosphole (**2c**).



1a: R = H
b: R = CH_3



2a: R = H; R' = Cl
b: R = CH_3; R' = Cl
c: R = CH_3; R' = Ph

Experimental Section

General Procedures. CH_2Cl_2, $CHCl_3$, CD_2Cl_2, and $CDCl_3$ were dried over P_2O_5 and stored over CaH_2. For some NMR samples the solvent was also predried by storage over samples of the compounds under study.

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† X-ray structural determinations.

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0020-1669/89/1328-0144$01.50/0

Table I. ^1H and ^{13}C NMR Data for 1,3,2-Benzodithiaphospholium Cations (**1a**,**b**), Dithiolium Cations (**4a**,**b**), 5-Chloro-1,3,2-benzodithiaphospholes (**2a**,**b**), Benzenedithiol, and Toluenedithiol

	(**1a**)$AlCl_4^-$	(**1b**)$AlCl_4^-$	(**1b**)$AlClBr_3^-$	**4a**[d]	**4b**[d]
^1H	8.25–7.32	8.54	8.43	8.90–7.95	8.73
	(AA′BB′X)[a]	8.46	8.35		8.00
		7.92	7.83		2.73
		2.72	2.66		
	$^3J_{HH}$ = 6 Hz	$^3J_{HH}$ = 8.5 Hz			
	$^4J_{HH}$ = 2.5 Hz				
	$^4J_{PH}$ = 1 Hz	*b*	*c*		
$^{13}C\{^1H\}$	149	153		145	
	131	150		132	
	128	144		128	
		133			
		128			
		127			
		22			

	2a[e]	**2b**[e]	$C_6H_6S_2$[e]	$C_7H_8S_2$[e]
^1H	7.70–7.29	7.55	7.39–7.07	7.26
		7.49		7.18
		7.12		6.87
		2.39		2.25
$^{13}C\{^1H\}$	138	139	131	137
	127	136	131	132
	126	128	128	131
		126		131
		126		127
		120		126
		21		21

[a] Simulated *J* values. [b] Meta *J* values not obtained. [c] *J* values not obtained. [d] Reference 29. [e] This work, thiol peaks omitted.

Ether was dried over $LiAlH_4$ and *n*-hexane over CaH_2. IR spectra were recorded as Nujol mulls or liquid films on CsI plates by using a Perkin-Elmer 283B spectrophotometer. NMR spectra were recorded on a Nicolet NT-360 spectrometer in $CDCl_3$, CD_2Cl_2 and CH_2Cl_2. Chemical shifts are reported in ppm relative to external standards (TMS for ^1H and ^{13}C, 85% H_3PO_4 for ^{31}P, and $Et_2O{\cdot}BF_3$ for ^{11}B). Mass spectra were obtained by using a CEC Model 21-104 mass spectrometer. Melting/decomposition points were recorded on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratories, Gottingen, West Germany. Dichlorophenylphosphine and sodium tetraphenylborate (Alfa Chemical Co.) were obtained commercially and used without further purification. Phosphorus trichloride, 1,2-benzenedithiol, and 3,4-toluenedithiol (Aldrich Chemical Co.) were distilled before use. Aluminum trichloride was multiply sublimed under a stream of nitrogen. 2-Chloro-1,3,2-benzodithiaphosphole (**2a**) and 2-chloro-5-methyl-1,3,2-benzodithiaphosphole (**2b**) were prepared by the literature method.[9] Reactions were performed in evacuated equal compartment vessels,[10] which were flame-dried before use.

Preparation of 1,3,2-Benzodithiaphospholium (1a) Tetrachloroaluminate. A solution of 2-chloro-1,3,2-benzodithiaphosphole (**2a**) (1.30 g, 6.3 mmol) in CH_2Cl_2 was poured in small portions onto $AlCl_3$ (0.84 g, 6.3 mmol) in CH_2Cl_2 (55 mL), maintaining maximum dilution of the reaction mixture with vigorous stirring. A bright yellow precipitate formed immediately under an orange solution. The mixture was stirred overnight at room temperature. The solution was filtered into the second bulb. The solid was then recrystallized by several back-distillations of the solvent, leaving a yellow crystalline solid in the second bulb. In this way the initial yellow precipitate was quantitatively transferred as a pure material into the second bulb. The sample was washed once and isolated by filtration. The solvent was removed in vacuo, and the yellow crystals were manipulated in the drybox and characterized as 1,3,2-benzodithiaphospholium (**1a**) tetrachloroaluminate: dec pt ~80 °C; yield 2.0 g, 5.8 mmol, 93%. Anal. Calcd for $C_6H_4AlCl_4PS_2$: C, 21.18; H, 1.18; P, 9.12; S, 18.82; Al, 7.94; Cl, 41.76. Found: C, 21.02; H, 1.22; P, 8.97; S, 18.71; Al, 8.15; Cl, 41.43. IR (ν_{max}, cm^{-1}): 1098 (m), 757 (s), 563 (m), 553 (m), 483 (s), 456 (m), 430 (m). Mass spectrum [*m*/*z* (relative intensity ^{35}Cl)]: 206 (28), 171 (100). ^{31}P NMR: 408 ppm. ^1H and ^{13}C NMR data are presented in Table I.

Table II. Crystallographic Data for $C_6H_4PS_2^+AlCl_4^-$ [(**1a**)$AlCl_4$] and $C_{13}H_{11}PS_2$ (**2c**)

	(**1a**)$AlCl_4$	**2c**
chem formula	$C_6H_4AlCl_4PS_2$	$C_{13}H_{11}PS_2$
fw	339.98	262.32
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	6.605 (3)	14.691 (3)
b, Å	23.377 (4)	6.291 (1)
c, Å	8.666 (2)	14.882 (3)
β, deg	100.28 (3)	114.56 (2)
V, Å^3	1316.5	1250.9
Z	4	4
T, °C	20	20
ρ_{calcd}, g cm^{-3}	1.713	1.393
μ, cm^{-1}	13.4	5.09
transmissn coeff	0.768–1.067	0.745–1.085
$R(F_o)$	0.036	0.037
$R_w(F_o)$	0.037	0.037
radiation	graphite-monochromated Mo Kα (λ = 0.70926 Å)	

Preparation of 5-Methyl-1,3,2-benzodithiaphospholium (1b) Tetrachloroaluminate. A solution of 2-chloro-5-methyl-1,3,2-benzodithiaphosphole (**2b**) (0.55 g, 2.5 mmol) in CH_2Cl_2 was poured in small portions onto $AlCl_3$ (0.36 g, 2.7 mmol) in CH_2Cl_2 (40 mL) with vigorous mixing. An orange solution formed immediately, and the $AlCl_3$ was taken into solution. The solution was stirred at room temperature overnight, and then approximately 70% of the solvent was removed. When the resulting solution was cooled to −10 °C, orange needlelike crystals formed, which were filtered and characterized as 5-methyl-1,3,2-benzodithiaphospholium (**1b**) tetrachloroaluminate (0.74 g, 2.1 mmol, 84%), dec pt ~106–108 °C. Anal. Calcd for $C_7H_6S_2PAlCl_4$: C, 23.73; H, 1.69; S, 18.08; P, 8.76. Found: C, 23.72; H, 1.83; S, 17.78; P, 8.83. IR (cm^{-1}): 815 (s), 722 (m), 565 (m), 555 (m), 540 (m), 505 (vs), 485 (vs), 465 (vs), 430 (m), 425 (m). Mass spectrum [*m*/*z* (relative intensity) ^{35}Cl]: 220 (29), 185 (100). ^{31}P NMR: 414 ppm. ^1H and ^{13}C NMR data are presented in Table I.

Preparation of 5-Methyl-1,3,2-benzodithiaphospholium Chlorotribromoaluminate. A solution of **2b** (1.00 g, 4.5 mmol) in CH_2Cl_2 was poured in small portions onto $AlBr_3$ (1.21 g, 4.5 mmol) in CH_2Cl_2 (40 mL) to give an orange solution, which was stirred at room temperature for ~2 h. Most of the solvent was removed, and a small amount of *n*-hexane was added. The solution was cooled to −10 °C and gave an orange microcrystalline precipitate of 5-methyl-1,3,2-benzodithiaphospholium chlorotribromoaluminate (1.03 g, 41%), dec pt ~ 75–78 °C. IR (cm^{-1}): 820 (s), 560 (m), 550 (m), 480 (vs). Mass spectrum [*m*/*z* (relative intensity; ^{35}Cl, ^{79}Br)]: 264 (1), 220 (26), 185 (100). ^{31}P NMR: 406 ppm. ^1H NMR data are presented in Table I.

Reaction of 2b with Molybdenum Pentachloride. A bright purple solid was isolated from the reaction of **2b** and $MoCl_5$ that has IR bands indicative of the presence of (**1b**)$MoCl_6^-$: 810 (m), 590 (s), 570 (s) cm^{-1}. Recrystallization of this material was unsuccessful.

NMR Studies of Reactions of 2b. The following small-scale (0.5 mmol in 10 mL of CH_2Cl_2) reactions of **2b** were studied by ^{31}P NMR: sodium hexafluorosilicate, no reaction; potassium hexachloromolybdate(III), no reaction; sodium tetraphenylborate, reacted to form **2c** and BPh_3.[11]

Preparation of 5-Methyl-2-phenyl-1,3,2-benzodithiaphosphole (2c). By the use of a modified literature procedure,[12] toluene-3,4-dithiol (2.09 g, 13.3 mmol) in ether (10 mL) was added dropwise under nitrogen to a well-stirred solution of dichlorophenylphosphine (2.40 g, 13.3 mmol) in ether (30 mL). A reaction occurred immediately with evolution of HCl, and the mixture was then stirred at room temperature for 1 h. The solvent was removed in vacuo to give a pale brown viscous oil, which dissolved in boiling *n*-hexane. On cooling, the mixture separated into two layers. However when the mixture was allowed to stand overnight at room temperature, clusters of lustrous white needlelike crystals formed at the junction of the layers and eventually all of the lower layer crystallized. The solvent was decanted, and the air-stable crystals were characterized as 5-methyl-2-phenyl-1,3,2-benzodithiaphosphole (**2c**) (3.3 g, 12.5 mmol, 94%), 55–58 °C. The identity and purity of the product were confirmed by ^{31}P, ^1H, and ^{13}C NMR spectra.

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X-ray Data Collection. Shiny block-shaped yellow crystals of (**1a**)-$AlCl_4$, suitable for crystallography, were obtained from a CH_2Cl_2 solution by slow removal of the solvent. A crystal was selected in the drybox and mounted in Pyrex capillary. A block-shaped crystal fragment of **2c** was carefully cut from one of the larger needlelike crystals grown from the bulk solution. The crystal was handled in the air and mounted in a glass capillary. All data were collected on an Enraf-Nonius CAD4 diffractometer. The crystal data are listed in Table II. The unit cell constants were obtained by least-squares analysis of the diffractometer setting angles of 25 well-centered reflections with $20° \leq 2\theta \leq 28°$. During the data collection the intensities of three standard reflections were monitored and showed no significant variation in intensity throughout both experiments.

Structure Solution and Refinement. The intensities were reduced to a standard scale by using routine procedures.[13] Corrections for Lorentz and polarization factors were applied. Absorption corrections[14] were applied for the data from **1a** but were not applied for those from **2c**. Scattering factors for neutral atoms[15] were corrected for the real part of the anomalous dispersion. The structures were solved by direct methods (MULTAN-80),[16] and refinements were carried out by using the SHELX-76 system.[17]

For (**1a**)$AlCl_4$, the systematically absent reflections confirmed the space group as $P2_1/c$. The positions of all heavy atoms were obtained from direct methods, and the carbon atoms were located from subsequent difference Fourier syntheses. The hydrogen atoms were placed geometrically with a C–H distance of 1.08 Å, and subsequent refinement of the hydrogen atoms without constraint conditions was successful. Final refinements were with anisotropic temperature factors on the non-hydrogen atoms and individual isotropic temperature factors on the hydrogen atoms. A two-block-matrix least-squares method was employed. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weight. No correction was applied for extinction. The highest peak in the final difference Fourier synthesis was 0.27 e $Å^{-3}$.

For **2c**, the systematically absent reflections confirmed the space group as $P2_1/n$. The positions of most of the non-hydrogen atoms were revealed by direct methods, and the remaining atoms, including hydrogen atoms, were located from a difference Fourier synthesis. All atom positions were refined without constraint except the methyl C–H bonds, which were loosely constrained at 1.08 Å. Refinement was performed in a manner analogous to that for **1a** and employed a three-block-matrix least-squares method. No correction was applied for extinction. The highest peak in the final difference Fourier synthesis was 0.29 e $Å^{-3}$. Final atomic coordinates and selected bond lengths and angles for **1a** and **2c** are listed in Tables III and IV, respectively.

Results and Discussion

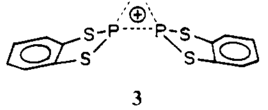
Dithiaphospholium Cation Synthesis. The versatile chloride ion abstraction reaction has been employed to obtain the first isolated example of a dicoordinate phosphorus cation possessing substituents other than second-row (nitrogen or carbon) elements.[18] Salts of the 1,3,2-benzodithiaphospholium cation (yellow) (**1a**)[1] and the tolyl analogue (orange) (**1b**) were isolated as extremely air-sensitive, crystalline solids from reactions of equimolar quantities of the corresponding precursor chlorophosphole and the chloride abstracting agents[19] $AlCl_3$, $AlBr_3$, and $MoCl_5$ in CH_2Cl_2.

The reactions of **2a**,**b** with $AlCl_3$ are very sensitive to the concentration of the chlorophosphole. At high concentration, a red solution is rapidly formed, which, upon workup, produces a substantial amount of unidentified red oil and a significantly reduced yield of the isolated salt of **1**. In contrast, at high dilution, a paler colored solution is formed, at a comparable rate, which produces an essentially quantitative yield of the salt. The red oil is reminiscent of the reaction mixture observed between benzene and $AlCl_3$ in CH_2Cl_2 and is attributed to electrophilic substitution products. However, **1** is not observed to react with $AlCl_3$. Moreover, the preference for chloride ion abstraction from **2a**,**b** over electrophilic substitution is expected to be independent of chlorophosphole concentration. On this basis, we postulate the formation of secondary multimolecular species, which are susceptible to aromatic electrophilic attack. In fact, cation **1** is observed by ^{31}P NMR spectroscopy to react with the precursor chlorophosphole **2a**,**b**, forming multimolecular Lewis adduct species containing P–P bonds, the simplest of which is viewed as **3**.[20] Such reactions have been reported for aminophosphenium cations.[21] The adducts may consist of more than one molecule of **2a**,**b** bound to a single molecule of **1**. In this environment, each

Table III. Fractional Atomic Coordinates and Isotropic Thermal Parameters for (**1a**) $AlCl_4$ and **2c** with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U(iso),[a] $Å^2$
		(a) $C_6H_4PS_2^+AlCl_4^-$ [(**1a**)$AlCl_4$]		
Al	0.0341 (2)	0.15120 (6)	0.2455 (2)	0.0449
Cl1	−0.0667 (2)	0.22221 (6)	0.3659 (2)	0.0664
Cl2	0.0669 (2)	0.07861 (6)	0.3945 (2)	0.0635
Cl3	−0.1792 (2)	0.13338 (6)	0.0381 (2)	0.0621
Cl4	0.3277 (2)	0.16987 (6)	0.1889 (2)	0.0701
S1	0.3402 (2)	0.31573 (6)	0.2356 (2)	0.0615
S2	0.6785 (2)	0.36935 (7)	0.0897 (2)	0.0740
P1	0.5540 (3)	0.29164 (7)	0.1096 (2)	0.0706
C1	0.3790 (7)	0.3887 (2)	0.2538 (5)	0.0494
C2	0.5345 (7)	0.4124 (2)	0.1871 (5)	0.0526
C3	0.5678 (8)	0.4720 (2)	0.1983 (7)	0.0751
C4	0.4438 (9)	0.5034 (2)	0.2729 (7)	0.0791
C5	0.2927 (9)	0.4799 (2)	0.3382 (7)	0.0796
C6	0.2530 (8)	0.4222 (2)	0.3325 (6)	0.0685
H3	0.689 (2)	0.4842 (13)	0.153 (2)	0.065 (2)
H4	0.463 (2)	0.5410 (14)	0.282 (2)	0.071 (2)
H5	0.196 (2)	0.4993 (13)	0.396 (2)	0.056 (2)
H6	0.135 (2)	0.4046 (13)	0.379 (2)	0.056 (2)
		(b) $C_{13}H_{11}PS_2$ (**2c**)		
P	0.8656 (1)	0.2952 (2)	0.4913 (1)	0.0553
S1	0.7937 (1)	0.1012 (2)	0.5576 (1)	0.0580
S2	0.75685 (9)	0.5365 (2)	0.45020 (9)	0.0532
C1	0.7273 (3)	0.2987 (7)	0.5894 (3)	0.0464
C2	0.7078 (3)	0.4927 (6)	0.5386 (3)	0.0431
C3	0.6450 (3)	0.6405 (7)	0.5532 (3)	0.0481
C4	0.6016 (3)	0.5991 (8)	0.6175 (3)	0.0562
C5	0.6236 (3)	0.4082 (9)	0.6686 (3)	0.0652
C6	0.6859 (3)	0.2595 (7)	0.6554 (3)	0.0559
C7	0.9696 (3)	0.4002 (6)	0.6002 (3)	0.0477
C8	0.9732 (3)	0.5963 (7)	0.6451 (3)	0.0524
C9	1.0562 (3)	0.6540 (7)	0.7274 (3)	0.0623
C10	1.1365 (3)	0.5209 (8)	0.7667 (3)	0.0623
C11	1.1339 (3)	0.3281 (8)	0.7227 (3)	0.0659
C12	1.0528 (3)	0.2703 (7)	0.6400 (3)	0.0581
C13	0.5328 (3)	0.7600 (8)	0.6326 (4)	0.0795
H3	0.6289 (15)	0.7626 (18)	0.5134 (16)	0.056 (2)
H5	0.5964 (15)	0.3789 (18)	0.7178 (16)	0.055 (2)
H6	0.7007 (15)	0.1208 (19)	0.6939 (16)	0.061 (2)
H8	0.9178 (15)	0.6818 (18)	0.6178 (15)	0.048 (2)
H9	1.0550 (16)	0.7979 (19)	0.7533 (16)	0.064 (2)
H10	1.1928 (15)	0.5438 (18)	0.8215 (16)	0.054 (2)
H11	1.1851 (16)	0.2494 (19)	0.7431 (16)	0.066 (2)
H12	1.0505 (15)	0.1342 (19)	0.6068 (16)	0.058 (2)
H131	0.5062 (17)	0.7010 (19)	0.6854 (17)	0.077 (2)
H132	0.4700 (16)	0.7858 (19)	0.5624 (17)	0.070 (2)
H133	0.5721 (17)	0.9080 (19)	0.6589 (17)	0.080 (2)

[a] For non-hydrogen atoms $U(\text{iso}) = (U_{11}U_{22}U_{33})^{1/3}$.



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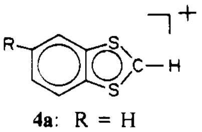

4a: R = H
b: R = CH_3

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(20) An NMR study of the reaction between **1** and **2** shows a broad signal with an intermediate chemical shift, dependent on the relative concentrations of the reactants. A detailed study of the chemistry of **1** is in progress, including reactions with a variety of Lewis bases.

(21) See, for example: Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994.

Table IV. Selected Bond Lengths (Å) and Angles (deg) for (**1a**)AlCl$_4$, **2c**, and Related Compounds Containing the C$_2$S$_2$P Heterocyclic Unit

	(**1a**)AlCl$_4$	**2c**	**8**[46]	**9**[48]	**10**[47]	**5**[35]
P-S1	2.016 (3)	2.110 (2)	2.08 (2)	2.051 (4)	2.087 (2)	2.180 (2)
P-S2	2.015 (3)	2.102 (2)				
C1-S1	1.728 (5)	1.761 (5)	1.828 (8)	1.82 (2)	1.75 (1)	1.765 (3)
C2-S2	1.711 (6)	1.765 (6)				
C1-C2	1.383 (7)	1.401 (6)	1.513 (8)	1.48 (2)	1.46 (3)	1.405 (3)
C1-C6	1.407 (8)	1.377 (8)				
C2-C3	1.411 (8)	1.389 (7)				
C3-C4	1.350 (10)	1.377 (8)				
C4-C5	1.351 (10)	1.386 (7)				
C5-C6	1.374 (9)	1.378 (8)				
S1-P-S2	97.59 (10)	94.9 (1)	83 (2)	100.5 (2)	98.5 (1)	92.3 (1)
P-S1-C1	102.6 (2)	99.1 (2)	106 (3)	96.0 (5)	99.4 (4)	99.7 (2)
P-S2-C2	102.5 (2)	99.6 (2)				
S1-C1-C2	117.8 (4)	118.8 (4)	109.9 (9)	113 (1)	119.1 (8)	119.6 (2)
S2-C2-C1	119.5 (4)	118.8 (4)				
S1-C1-C6	120.2 (4)	121.6 (4)				
S2-C2-C3	121.4 (4)	121.0 (4)				
C1-C2-C3	119.1 (5)	120.0 (5)				
C2-C3-C4	118.0 (6)	120.8 (4)				
C3-C4-C5	122.6 (6)	118.4 (5)				
C4-C5-C6	122.3 (6)	121.8 (6)				
C5-C6-C1	116.0 (6)	119.8 (5)				
C6-C1-C2	122.1 (5)	119.3 (5)				

of the bound units of **2a,b** is more relunctant to release a chloride ion than the free neutral chlorophosphole **2a,b**, due to the effect of the emcumbent cationic charge. Consequently, the aromatic electrophilic attack becomes more competitive. At high dilution the adduct formation is reduced, thereby reducing the electrophilic substitution and improving the yield of the cation to essentially quantitative proportions. AlBr$_3$ effects a similar rapid chloride ion abstraction from **2b** to produce the corresponding yellow salt of **1b**, which has been characterized spectroscopically. No reaction was observed with sodium hexafluorosilicate or potassium hexachloromolybdate(III). A slow reaction of **2b** with sodium tetraphenylborate produced **2c** in high yield together with BPh$_3$. This is clearly the result of an electrophilic substitution of the boron from a phenyl group of BPh$_4^-$ by the phosphorus center. The quantitative nature of this reaction implies a concerted process that avoids the discrete formation of the highly reactive cation **1b**.

Spectroscopic Characterization. A comparison of the infrared spectra of salts of **1** with those of the precursor chlorophosphole **2a,b** indicates some dramatic structural adjustments upon chloride ion abstraction. The spectra of all salts of **1b** are very similar except for the bands corresponding to the respective anions, at 485 cm^{-1} for AlCl$_4^-$[22a] and 480 cm^{-1} for AlClBr$_3^-$.[22b] The absence of bands at 622 and 320 cm^{-1}, corresponding to AlCl$_3$,[22a] is consistent with the formation of AlCl$_4^-$ (AlBr$_3$, 373 and 341 cm^{-1}).[22a] P–Cl stretching frequencies[23,24] for **2a** (415 cm^{-1}) and **2b** (405 cm^{-1}) are also clearly absent in the spectra of salts of **1**. The strong absorption at 760 cm^{-1} for (**1a**)AlCl$_4$ is readily attributable to the C–H out-of-plane deformations of the four adjacent aromatic hydrogens, also observed as a strong band at 743 cm^{-1} for **2a**. For **1b** the bands due to the 1,3,4-substitution pattern occur between 810 and 815 cm^{-1}.[24] Tentative assignment of bands due to the P–S linkages of **1** are made by comparison with related systems. The infrared spectrum of a matrix-isolated sample of S═P—Cl contains a sharp, strong absorption at 716.1 cm^{-1}, which is assigned to the P═S stretching vibration.[25] Phosphorus(V) sulfides that possess one or more terminal P═S units (e.g. P$_4$S$_{5,7,10}$) all show strong absorptions in the 690–650-cm^{-1} region, while the lowest sulfide, P$_4$S$_3$, contains no P═S linkages and consistently shows no appreciable absorption in this region.[23,24] Cation **1a** exhibits peaks between 665 and 525 cm^{-1}, which may be due to the S–P–S moiety, and **1b** shows absorptions between 690 and 535 cm^{-1}, which are essentially independent of the anion. While the P—S vibrations may be coupled to the C—S modes, the intermediate position of these peaks between those identified for the P—S single and P═S double bonds may be associated with a degree of multiple bonding between phosphorus and sulfur.

The mass spectra of the tetrachloroaluminate salts of **1** are essentially identical with those of their corresponding chlorophospholes **2a,b**. As observed for other salts of non-metal cations,[26] a halide ion reabstraction by the cation from the anion occurs in the mass spectrometer source. Decomposition of **1** in the mass spectrometer source is to be expected, as the compounds have decomposition points of ~80 and 110 °C, respectively, while the source temperature employed in the spectrometer was 140 °C. Interestingly, the mass spectrum of (**1b**)AlClBr$_3$ reveals a reabstraction of both Cl$^-$ and Br$^-$ from the anion, but is otherwise identical with that of **2b**. Minimal fragmentation of the base peaks was observed for an ionization voltage of 70 eV, implying high gas-phase stability for cation **1**.[27]

Table I presents a comparison of ^{1}H and ^{13}C NMR data for derivatives of **1** and those of related systems. The ^{1}H NMR spectrum of **1a** has been simulated as an AA′BB′X system. In general, significant deshielding, with respect to the parent chlorophospholes and dithiols, is observed in the ^{1}H and ^{13}C NMR spectra for the carbocyclic frameworks of **1**. This implies effective delocalization of the molecular charge into the benzo unit, presumably via the π-system. σ-Induction does not result in such dramatic shifts on the nuclei of aromatic moieties.[28] In fact, the ^{1}H and ^{13}C chemical shifts are very similar to those of the benzodithiolium **4** systems, which are regarded as aromatic.[29] In this context, the heteroatoms of **1** can be viewed as an integral part of a 10-π-electron (Hückel) system. The aromatic behavior is further demonstrated by noting that the shift trends observed for **1b** with respect to **2b** are related to those of 2-methylnaphthalene with respect to toluene. The magnetic anisotropic

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(28) See, for example, ^{1}H NMR spectra of (PhO)$_3$P and (PhO)$_3$PMeI in: Pouchart, C. J. *The Aldrich Library of N.M.R. Spectra*, 2nd ed.; Aldrich: Milwaukee, WI, 1983; Vol. 2.

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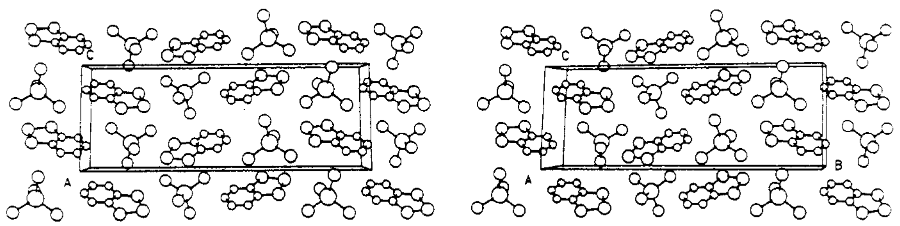


Figure 1. Stereoview of a unit cell packing for (**1a**)$AlCl_4$.

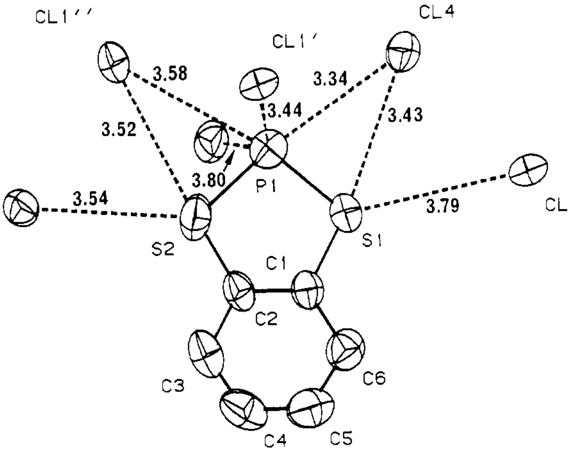


Figure 2. View of cation **1a** showing the anion contacts, less than 3.8 Å. Atoms Cl1, Cl4, Cl1'', and Cl2'' are in the plane of the cation.

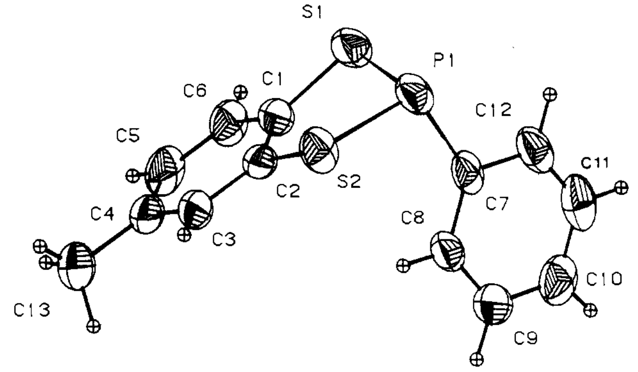


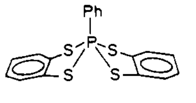
Figure 3. Thermal ellipsoid plot of **2c**.

effect of 10 π-electrons is greater than that of 6 π-electrons,[30] producing a greater deshielding for all organic centers. This is apparent for the protons; however, the large chemical shift range of ^{13}C precludes the observation of the effect on the methyl carbon nucleus. Consistently, the methyl protons of **1b** show a dramatic relative chemical shift with respect to **2b**, while the relative difference for the methyl carbon center is very small.

The characteristic ^{31}P chemical shifts for most aminophosphenium ions are approximately 100 ppm deshielded from the corresponding precursor chlorophosphole.[18] By comparison, the chemical shifts observed for **1** are more than 200 ppm deshielded, perhaps demonstrating the relative ineffectiveness of sulfur to π-donate by comparison with nitrogen. The signal shape is temperature dependent, very broad at room temperature and sharp at −80 °C. We associate this behavior with a rapid equilibrium process involving one of two possible processes, which may be related. A reversible reabstraction of Cl^- by the cation to re-form **2a**,**b** and $AlCl_3$ in solution is consistent with the mass spectral data. Alternatively, a cation–anion association may occur in solution, consistent with the solid-state structure. Secondary peaks of relatively low intensities appear with time for all samples, the largest of which is at 218 ppm. The appearance of this signal is most facile for the $AlClBr_3^-$ salt and is probably due to decay of the cation in solution.

Crystal and Molecular Structure of 1,3,2-Benzodithiaphospholium (1a) Tetrachloroaluminate. A packing diagram of 1,3,2-benzodithiaphospholium (**1a**) tetrachloroaluminate is presented in Figure 1.[31] Although the structure is composed of discrete cationic and anionic units, anion–cation contacts are the foundation of a macrostructure consisting of layers, 11.6 Å wide, that run perpendicular to the *b* axis of the unit cell (Figure 1). All of the cation/anion interactions occur within this layer between the chlorine atoms of the anion and the heteroatoms of the cation, as illustrated for a single cationic unit in Figure 2. The layer is bounded by the benzo groups of the cations. Similar contacts have been reported for the salts of a number of homopolyatomic non-metal cations, and are believed to be nucleophilic, charge-transfer interactions.[32] The S–P–S unit of the cation can be regarded as isolobal[33] to any three atom segment of a Ch_4^{2+} cation (Ch = S, Se, Te). Moreover, the five-membered ring of the cation is isovalent with Ch_4^{2+}. Consistent with this analogy, the arrangement of the contacts around **1a** is very similar to that observed for Ch_4^{2+} tetrachloroaluminate salts.[32a]

Cation **1a** is planar with a maximum deviation from the plane at phosphorus of 0.027 Å. The sulfur–phosphorus bond lengths (mean 2.016 (2) Å) are significantly shorter than those of related molecules containing "single" P–S bonds. Although compounds such as P_4S_3 (mean P–S = 2.09 (1) Å)[34] involve cage and ring strain features and the spirocyclic phosphorane **5** (mean P–S =



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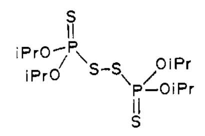

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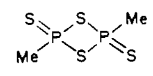

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2.180 (2) Å)[35] contains phosphorus(V), they serve to illustrate a heterocyclic P–S single-bond distance that is independent of the gross molecular features. Acyclic compounds, such as $P_2S_4(i\text{-}C_3H_7O)_4$ (**6**) (mean P–S = 2.072 (2) Å),[36] contain P–S bonds, which may be regarded as archetypal single P–S bonds. The slight lengthening of the P–S bonds observed in cyclic compounds can be attributed to the strained geometry imposed by the ring environment, further illustrated by the four-membered ring system, $P_2S_4(CH_3)_2$ (**7**), which has an even longer P–S bond (2.141 (6) Å).[37] Phosphorus(V) sulfides, such as P_4S_{10}, contain very short P=S bonds (mean 1.908 (8) Å) by virtue of $3d\pi$–$3p\pi$ bonding and long P—S single bonds (mean 2.097 (8) Å).[38] The P–S bond

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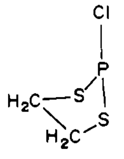
length observed in **1a** is intermediate between the average single bond and the P=S double bond of the phosphorus(V) sulfides. To our knowledge **1a** contains the shortest P(III)–S bond yet reported. Although the S–P–S bond angle is small compared with that observed for acyclic phosphenium ions, it is almost identical with that observed for some cyclic aminophosphenium cations[18] and is probably required by the cyclic geometry.

The carbon–sulfur bonds (mean 1.719 (4) Å) of **1a** are also substantially shorter than a single C–S bond (e.g. dimethyl sulfide, 1.802 (2) Å)[39] and are comparable with that observed in thiourea (1.71 (1) Å),[40] a molecule in which there is substantial π-electron delocalization. Clearly, there is significant π-interaction between the sulfur centers and the benzo moiety in **1a**. Unfortunately, the errors in the C–C bond lengths are too large to allow one to make definitive conclusions regarding the structural trends of the benzo moiety.

Crystal and Molecular Structure of 2c. A SNOOPI[31] representation of the molecular structure of **2c** is presented in Figure 3. The structure is composed of discrete molecular units, which are folded (25.2°) about the S–S vector. The dithiobenzene moiety is essentially planar (maximum deviation from the plane is 0.11 Å at S1), with the phosphorus center displaced from this plane by 0.53 Å. A distorted tetrahedral geometry at the phosphorus center implies the presence of a stereochemically active lone pair. The phosphorus–sulfur bond lengths are similar to those in P_4S_3,[34] further demonstrating the general uniformity of the P–S single bond length at 2.1 Å. The P–C bond length (1.827 (4) Å) is comparable with those determined for triphenylphosphine (1.822 (5)–1.831 (5) Å)[41] and marginally shorter than those in trimethylphosphine (1.846 (3) Å).[42] The two P–C–C angles are not equal and are close to the values obtained for triphenylphosphine [124.0 and 116.1° (average values)]. This inequality is possibly steric in origin and is observed in many compounds containing a P–Ph unit, especially where the phosphorus center is tricoordinate.[43] The C–C bond lengths of the benzo moiety are not significantly different. The phenyl group is twisted such that one of the ortho hydrogens of the phenyl group lies almost directly above one of the sulfur atoms. The S2–P–C7–C8 torsion angle is 1.0 (7)° and is directed toward the sulfur atom closest to the methyl group of the benzo unit. The contact distance between sulfur and hydrogen is 2.8 Å, within the sum of the van der Waals radii (1.85 and 1.3 Å, respectively). We believe that this conformation is the result of a simple packing feature of the molecule, since the ortho carbon nuclei are equivalent in solution (^{13}C NMR).

Structure and Bonding in 1 and 2. The stability and conformation observed for the aminophosphenium cations is attributed to the optimization of π-bonding by means of donation of the lone pairs from the nitrogen centers into the formally vacant 3pπ orbital of the phosphorus.[18,44] Consequently, the P–N bonds in these compounds are relatively short ($[((CH_3)_2HC)_2N]_2P^+$ mean P–N = 1.613 (4) Å).[44] Although P–N single bonds are known to vary dramatically depending on the oxidation state and the chemical environment of the phosphorus and nitrogen centers, they are usually longer than 1.68 Å.[45] Consistent with the isolobal[33] relationship between an amine group and a dicoordinate sulfur center, a similar order of shortening is observed for the P–S bond in the dithiaphospholium cation **1a**, with respect to a "single" P–S single bond. While the molecular charge may be partly responsible for the shortening, the structural and spectroscopic evidence supports a fully charge delocalized system. Moreover, the molecular planarity and general aromatic behavior of **1** are clearly indicative of a bicyclic 10-π-electron system. Compound **2c** represents the closest PS_2 σ-bonded analogue of **1**, allowing a direct structural comparison. In this context, the stereochemical presence of the lone pairs on the phosphorus and the sulfur centers evident in the folded conformation of **2c** is absent in the planar structure of **1a**. The P–S bond of **1a** is 4% shorter than that in **2c**. Moreover, the substantially shorter C–S bonds in the cation illustrate an integrated π-network for **1**, requiring 3pπ–3pπ bonding between phosphorus and sulfur.

Relevant bond lengths and angles observed for related compounds (**5**, **8**–**10**) containing the C_2S_2P heterocyclic unit are compared with those of **1a** and **2c** in Table IV. Except for cation **1a** the compounds listed are all severely puckered, with the phosphorus atom displaced from the C_2S_2 plane. The spirocyclic phosphorane[35] **5** contains an aromatic moiety and represents the closest example to **1a** and **2c**. The geometry around the phosphorus center of **5** is distorted square pyramidal. In general, the bond lengths and angles of the heterocycles are similar to those of **2c**, despite the 5-coordination and higher oxidation state of the phosphorus center in **5**. In fact, the angles at P and S in all the compounds in Table IV fall in a narrow range (S–P–S, 91–100°; P–S–C, 96–106°) except for **8**,[46] in which the electronegative nature of the chlorine substituent probably enhances the stereochemical presence of the lone pair on the phosphorus center. The degree of saturation at the carbon centers is reflected in the bond lengths, and cation **1a** is the extreme case with a very short ring fusion bond. The C–S bonds of **1a** and **2c** are relatively short, demonstrating a π-interaction of the sulfur centers with the benzo moiety. All P–S bonds are significantly longer than those of **1a**, and the range of lengths is worthy of note. Compounds **5** and **2c** contain relatively long P–S bonds, with those of **8** and **10**[47] slightly shorter. The shortening in **8** may again be due to the electronegative influence of the chlorine atom. π-Participation of d orbitals is likely responsible for the slight shortening in **10**, and the effect is enhanced in **9** by virtue of the electronegative chlorine atom.[48]



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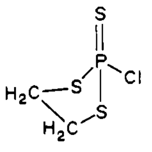

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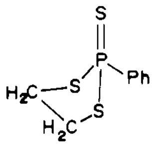

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π-Bond Strength and Stability. The nitrogen derivative of **1** is a stable ionic system as the halide salt.[49] The structure adopts the same naphthalenic geometry; however, it does not require the presence of a weakly basic anion. The preference for π-bonding demonstrated by nitrogen precludes the formation of a covalent N–Cl bond, while the preference for σ-bonding for the heavier elements such as phosphorus requires some competition for the chloride ion, by a Lewis acid, in order to stabilize the σ-bonded arrangement. The discovery of a thermodynamically stable 3pπ–3pπ bonding in the first phosphorus(III)–sulfur cation is the foundation of a potentially comprehensive π-chemistry for the heavier non-metals. The theoretical and experimental energetic studies of Schmidt and Gordon recognize the full P=S π-bond as relatively strong in comparison with Si=Si and P=P,[5] both of which have been isolated by means of kinetic stabilization. Moreover, the P=S π-bond is calculated to be significantly weaker than the Si=S bond. On this basis, we are currently investigating the potential synthesis of silicon analogues of **1** as examples of

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systems possessing delocalized π-bonding between Si and S.

Conclusions

A combination of four principle factors are responsible for the thermodynamic stability of the π-bonded cation **1**.

(1) The positive charge enhances π-overlap and renders alternative π-bonded frameworks unfavorable, due to localization of charge on adjacent atoms.[8]

(2) The 10-π-electron count provides an inherent aromatic stabilization in addition to an efficient delocalization of the positive charge.

(3) Low basicity of anions, such as $AlCl_4^-$, prevents donation to the cation and subsequent covalent bond formation.[7] Nevertheless, the long-range nucleophilic contacts observed in the solid state are indicative of a degree of donation.

(4) The crystal lattice energy of the salt is expected to be greater than that of an alternative covalent Lewis adduct structure ($\mathbf{2}\cdot AlCl_3$). Although the energy difference may be small, it plays a significant role in the solid-state stability of the system, as demonstrated by the labile solution behavior.

The energy of the CC π-bond is only slightly less than that of the CC σ-bond, and this has been identified as one of the factors reponsible for the diverse and extensive chemistry of carbon.[4] The stabilizing features for the PS π-bond listed above represent a contribution toward general stable heteroatomic π-bonding, which is energetically competitive with the respective σ-bonding. Such a development has significant consequences in terms of the advancement of the chemistry of the non-metals as a whole. There is now potential for the synthesis of π-bonded systems containing many new combinations of the heavier non-metals.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (N.B. and T.S.C), the donors of the Petroleum Research Fund, administered by the American Chemical Society (N.B.), and Dalhousie University for financial support, Dr. D. L. Hooper and the Atlantic Regional Magnetic Resonance Center for obtaining the NMR spectra, and Patrick Cho for help in preparing (**1b**)$AlClBr_3$.

Supplementary Material Available: Tables SI–SVI, listing crystallographic data, anisotropic thermal parameters, bond lengths and angles, contact distances, torsion angles, and least-squares plane calculations for $C_6H_4PS_2^+\ AlCl_4^-$ [(**1a**)$AlCl_4$] and $C_{13}H_{11}PS_2$ (**2c**), Table SIX, listing mass spectral and infrared data, and Figure S1, showing the contacts between anions and the cation (12 pages); Tables SVII and SVIII, listing observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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Synthesis of the New Organic Metal $(ET)_2C(CN)_3$ and Characterization of Its Metal–Insulator Phase Transition at ~180 K

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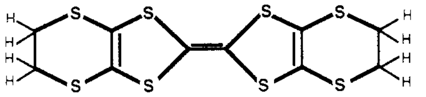
Received March 17, 1988

A new conducting salt $(ET)_2C(CN)_3$, the first 2:1 salt of ET (i.e., bis(ethylenedithio)tetrathiafulvalene) with a planar-triangular anion, was synthesized, and its structure was determined by single-crystal X-ray diffraction. Crystal data for $(ET)_2C(CN)_3$ are as follows: monoclinic, $P2/a$, $Z = 2$; at 125 K/298 K, a = 14.684 (8)/14.979 (7) Å, b = 6.667 (3)/6.700 (2) Å, c = 16.400 (6)/16.395 (4) Å, β = 95.13 (3)/94.80 (3)°, and V_c = 1599 (1)/1639.7 (9) Å^3. The electrical conductivity of this salt as a function of temperature shows that it undergoes a metal–insulator phase transition at ~180 K. The magnetic susceptibility measured as a function of temperature and the tight-binding band electronic structure calculated for $(ET)_2C(CN)_3$ show that the phase transition at ~180 K is a Peierls type metal–insulator transition. The band electronic structure of $(ET)_2C(CN)_3$ predicts a doubling of the b axis as a consequence of the Peierls distortion, which has been confirmed by the use of X-ray photographs of $(ET)_2C(CN)_3$ taken as a function of temperature.

The donor molecule bis(ethylenedithio)tetrathiafulvalene (**1**). (BEDT-TTF or simply ET) is the source of numerous salts of type $(ET)_mX_n$ with mononegative ions X^-.[1] Of the several 2:1 salts produced with linear anions, only the β-phase salts, β-$(ET)_2X$, with $X^- = I_3^-$, AuI_2^-, and IBr_2^- give rise to ambient-pressure superconductors (T_c = 1.4,[2] 5.0,[3] and 2.8 K[4] for $X^- = I_3^-$, AuI_2^-, and IBr_2^-, respectively). Recently, a 2:1 salt, $(ET)_2Cu(SCN)_2$, with a bent anion has been found to be an ambient-pressure superconductor, but with a much higher transition temperature (T_c = 10.4 K).[5] ET salts with planar-triangular anions are rare, the only examples being α, β, and γ phases with NO_3^-.[6] In the present study, we report the synthesis of $(ET)_2C(CN)_3$, the first 2:1 salt with a planar-triangular anion, and its crystal structure as determined by single-crystal X-ray diffraction. Electrical conductivity of $(ET)_2C(CN)_3$ measured as a function of temperature indicates that this salt undergoes a broad metal–insulator (MI) transition near 180 K. We have characterized this phase transition by measurements of the magnetic susceptibility and by



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