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Synthesis, Properties, and Bishomoaromaticity of the First Tetrahalogenated Derivative of a 1, 5-Diphosphadithiatetrazocine: A Combined Experimental and Computational Investigation

Tristram Chivers,*,[†] Robert W. Hilts,[‡] Peng Jin,[§] Zhongfang Chen,*,[§] and Xin Lu*,[∥]

[†]*Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4, Canada,* [‡]*Faculty of Arts and Science, Grant MacEwan University, City Center Campus, 10700-104 Avenue, Edmonton, Alberta T5J 4S2, Canada,* [§]*Department of Chemistry, Institute for Functional Materials, University of Puerto Rico, San Juan, PR 00931, and* [∥]*State Key Laboratory for Physical Chemistry of Solid Surfaces, Center for Theoretical Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China*

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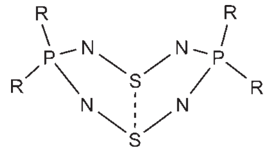
The first example of a tetrahalogenated derivative of a diphosphadithiatetrazocine, 1,5-$Cl_2P(NSN)_2PCl_2$ (**3**), was synthesized by cyclocondensation of a 2:1 mixture of SCl_2 and SO_2Cl_2 with $Cl_2P(NSiMe_3)N(SiMe_3)_2$ in CH_2Cl_2. The heterocycle **3** was isolated as an orange, moisture-sensitive, thermally labile solid and characterized by mass spectrometry, ^{31}P NMR, and UV−visible spectroscopy. The low-field ^{31}P NMR chemical shift (93.7 ppm) is indicative of a cross-ring S—S interaction in the eight-membered $P_2N_4S_2$ ring, and this conclusion is supported by density-functional computations. Compound **3** exhibits unusual physical properties compared with those of the known tetraalkyl or aryl derivatives; mild heating (90 °C) produces an orange rubbery material. The bishomoaromatic character of the diphosphadithiatetrazocine 1,5-$R_2P(NSN)_2PR_2$ (R = Me, Cl, F) is evinced by the negative nucleus-independent chemical shift (NICS) values, and the through-space bishomoconjugation in the eight-membered ring decreases with increasing electronegativity of the substituents attached to the P atoms.

Introduction

Diphosphadithiatetrazocines $R_2P(NSN)_2PR_2$ are eight-membered rings that may be considered as hybrids of the well-known cage molecule S_4N_4[1] and monocyclic cyclotetraphosphazenes $(R_2PN)_4$.[2] The isomer 1,5-$Me_2P(NSN)_2PMe_2$ was first obtained in 1982 via decomposition of the six-membered ring $(Me_2PN)(SN)_2$, which was prepared by the reaction of S_4N_4 with Me_2PPMe_2.[3] Subsequently, improved syntheses for a variety of derivatives of the type 1,5-$R_2P(NSN)_2PR_2$ (**1**, R = Me, Et, Ph) were reported.[4,5] These 1,5-diphosphadithiatetrazocines are colorless, air and thermally stable solids. In the solid state they adopt a folded (bicyclic) structure as a result of a transannular S---S interaction in the range of 2.43−2.55 Å (cf. 2.06 Å for an S−S single bond in *cyclo*-S_8) and this conformation is retained in solution.[3,4,6] As a consequence, derivatives in which the two substituents on phosphorus differ, for example, 1,5-$RR'P(NSN)_2PRR'$ (R = Me, R′ = Ph; R = Cl, R′ = CCl_3), form three structural isomers.[4b] In the latter case the predominant isomer, which has the two Cl substituents in *endo* positions (**2**), has been structurally characterized.[4b,5]



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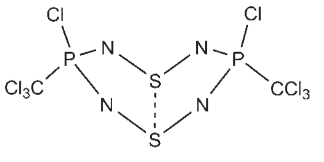

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1,5-Diphosphadithiatetrazocines serve as excellent models for elucidating the initial outcome of reactions of sulfur−nitrogen compounds. The folded rings **1** exhibit ^{31}P NMR

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*To whom correspondence should be addressed. E-mail: chivers@ucalgary.ca (T.C.), zhongfangchen@gmail.com (Z.C.), xinlu@xmu.edu.cn (X.L.). Fax: (+1)403-289-9488 (T. C.). Phone: (+1)403-220-5741 (T. C.).

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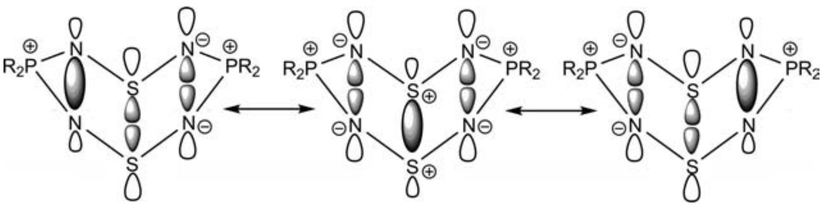
Scheme 1



chemical shifts at anomalously low fields (100−140 ppm), compared to those of cyclophosphazenes, both in the solid state and in solution.[4b,6] Consequently, ^{31}P NMR spectroscopy provides an informative method of monitoring reaction progress and inferring the loss or retention of the cross-ring S---S interaction. In contrast to the lability of the S_4N_4 cage,[1] the integrity of the eight-membered ring is retained upon treatment of **1** with either electrophiles or nucleophiles. For example, the 1,5-isomer behaves as a weak Lewis acid in forming N-bonded adducts with protic or Lewis acids[7] and with platinum(II);[8] the S---S contact is maintained in these adducts. The oxidative addition of halogens to **1** (R = Ph) produces the *exo, endo* dihalogenated derivatives 1,5-R_2P-(NS(X)N)$_2$PR_2 (X = Cl, Br).[9] The latter have been used as a source of the dication $[Et_2P(NSN)_2PEt_2]^{2+}$, which is a planar eight-membered ring.[10] The $P_2N_4S_2$ ring in **1** is also readily susceptible to nucleophilic attack at sulfur; reactions with organolithium reagents produce the dimeric adducts $[Li\{(Ph_2P)_2N_4S_2R)\}]_2$.[11] Alkali-metal derivatives of the dianion $[(Ph_2P)_2N_4S_2]^{2-}$ may also be prepared by the reaction of **1** (R = Ph) with M[Et_3BH].[12] The combination of hard (*N*) and soft (*S*) coordination sites confers **1** with a versatile coordination chemistry.[13] The formation of η^2-S,S′ complexes with platinum are of particular interest in view of a bonding analogy with η^2-alkene complexes.[14]

1,5-Diphosphadithiatetrazocines have also attracted continuing theoretical interest related to the nature of the S---S interaction, which arises from the in-phase overlap of high-lying N=S=N π* orbitals.[3] Early approximate density functional theory (DFT) calculations for 1,5-Me_2P(NSN)$_2$PMe_2 estimated the S---S bond energy to be 133 kJ mol^{-1},[15] and a subsequent DFT calculation at the B3LYP level for the model system 1,5-H_2P(NSN)$_2$PH_2 concluded that the bond order is about 0.7.[16] Very recently, renewed attention to the bonding in these fascinating bicyclic compounds have led to their classification as inorganic examples of bishomoaromatic 6c-10e molecules as a result of the through-space interaction (homoconjugation) of two 3c-5e π-bonds of the (NSN)$^-$ subunits (see Scheme 1 for depiction of the three valence-bond structures that contribute to this interaction).[17] An alternative description of **1** as trishomoaromatic molecules has subsequently been suggested.[18]

In the context of the current interest in the unsaturated, bicyclic $P_2N_4S_2$ system, we report the synthesis of 1,5-Cl_2P-(NSN)$_2$PCl_2 (**3**), the first example of a tetrahalogenated derivative of a 1,5-diphosphadithiatetrazocine. The influence of the electronegative substituents attached to phosphorus on the structure, physical properties, and reactivity of this eight-membered ring system were of primary interest. In addition, the use of **3** as a precursor for the polymer $(Cl_2PNSN)_x$ via ring-opening polymerization was an intriguing possibility, since this putative PNSN backbone polymer is a hybrid of the well-known inorganic polymers $[Cl_2PN]_x$[2] and $[SN]_x$,[1] which are elastomeric and conducting materials, respectively.[19] Complementary quantum chemistry computations have been carried out for **3**, as well as the unknown fluorine analogue 1,5-F_2P(NSN)$_2$PF_2 (**4**), to provide structural information and in an attempt to explain the unusual properties of the tetrachlorinated derivative **3**.

Experimental Section

Reagents and General Procedures. The reagent $Cl_2P(NSiMe_3)$-$N(SiMe_3)_2$ was prepared by the published procedure.[20] The reagents SCl_2 and SO_2Cl_2 were obtained from Aldrich. SCl_2 was purified by vacuum distillation (ca. 1 Torr.) from PCl_5 and then used immediately to minimize disproportionation into S_2Cl_2 and Cl_2. SO_2Cl_2 was freshly distilled before use. Dichloromethane was dried, distilled, and purged with argon for 20 min immediately prior to use.

Physical Techniques. $^{31}P\{^1H\}$ NMR spectra were recorded for CH_2Cl_2 or tetrahydrofuran (THF) solutions on a Bruker AM 400 spectrometer operating at 161.978 MHz . Electron-impact mass spectra (70 eV) were obtained by using a Kratos MS80RFA instrument. UV−visible spectra were measured with a Cary 50 spectrophotometer. Chemical analyses were performed by the Canadian Microanalytical Service, Vancouver, BC, Canada.

Synthesis of 1,5-Cl_2P(NSN)$_2$PCl_2 (3). A golden yellow solution of a mixture of SCl_2 (0.812 g, 7.89 mmol) and SO_2Cl_2 (0.540 g, 4.00 mmol) in dichloromethane (30 mL) at 0 °C was added dropwise over 30 min to a clear, colorless solution of Cl_2P-$(NSiMe_3)N(SiMe_3)_2$ (2.79 g, 8.00 mmol) in dichloromethane (50 mL) at 0 °C. The reaction mixture was stirred for 1 h at 23 °C, and then the volume of solvent was reduced to 20 mL under vacuum. The concentrated orange solution was filtered to remove a small amount of yellow precipitate, and the clear filtrate was then added

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[19] A hybrid polymer composed of alternating [NPMe_2] and [NS(O)R] groups (i.e. sulfur(VI) atoms) has been prepared by a condensation process. See: Chunechom, V.; Vidal, T. E.; Adams, H.; Turner, M. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 1928.

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by cannula to a Schlenk vessel containing rapidly stirred cold *n*-hexane (30 mL at −5 °C). This procedure initially produced a yellow precipitate which, by the end of the addition, had transformed to an orange oil. The volume of the solvent was reduced to about 5 mL under vacuum affording a viscous orange solid and a pale yellow supernatant. The supernatant was discarded, and the residual gummy orange solid was kept under dynamic vacuum overnight giving 1,5-$Cl_2P(NSN)_2PCl_2$ (**3**) (0.883 g, 2.73 mmol, 68%) as a free-flowing orange powder. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 23 °C): δ 93.7 (s). EIMS (70 eV): *m*/*z* 323.7 (M^+, 42%), 277.8 ($[M - SN]^+$), 8%, 64.1 (S_2^+, 100%). UV−vis (CH_2Cl_2, nm): λ_{max} 270 (s), 445 (vw). Anal. Calcd for $Cl_4N_4P_2S_2$: Cl, 43.78; N, 17.30; S, 19.80%. Found: Cl, 41.26; N, 16.06; S, 25.61%. The analytical data correspond to the expected atomic ratio of Cl:N = 1.02:1, but the high sulfur content indicates the presence of about 7% of *cyclo*-S_8.

Thermolysis of 1,5-$Cl_2P(NSN)_2PCl_2$ (3). Samples of **3** (ca. 0.500 g) in a sealed, evacuated Pyrex tube were heated at temperatures in the range 80−120 °C for time periods ranging from 1 to 16 h. Upon cooling to room temperature, the soluble products were extracted with THF, 1,4-dioxane, or DMF and analyzed by ^{31}P NMR spectroscopy. The details of these spectra are given in the Results and Discussion section.

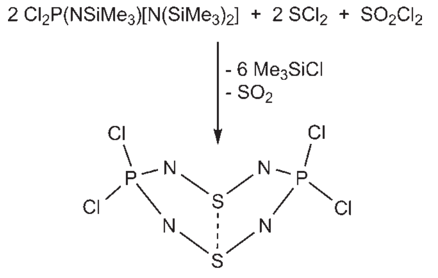
Computational Details. The full geometry optimizations followed by harmonic vibrational computations were performed at the B3LYP/6-311+G(3df) level of theory.[21,22] The nucleus-independent chemical shifts (NICS),[23,24] a simple and efficient probe of aromaticity, were computed at the center of the $(NSN)_2$ portion of the systems under investigation, using the same theoretical level as the geometry optimizations. The NICS out-of-plane *zz* tensor component, a superior NICS index for planar systems,[25] was also examined. Significantly negative NICS values indicate the presence of induced diatropic ring currents or "aromaticity", whereas positive NICS values denote paratropic ring currents or "antiaromaticity". The Gaussian 03 package was employed throughout our density functional theory (DFT) computations.[26]

To gain more insights into the nature of the intramolecular interactions, especially the cross-ring S−S bonding, a quantum theory of atoms in molecules (QTAIM) study on the above B3LYP/6-311+G(3df) geometries and wave functions was performed using AIM2000 software.[27] The 3D molecular orbitals and electron densities (see Supporting Information) were visualized with the aid of gOpenmol program.[28]

Results and Discussion

Preparation and Spectroscopic Characterization of 1,5-$Cl_2P(NSN)_2PCl_2$ (3). 1,5-Diphosphadithiatetrazocines are best prepared by cyclocondensation reactions of the readily available reagents $R_2P(NSiMe_3)N(SiMe_3)_2$ (R = alkyl, aryl) or the lithium reagent $Li[Ph_2P(NSiMe_3)_2]$ with SCl_2 or $SOCl_2$.[3,4] The lithium reagent gives higher yields, and the products are more easily purified since, in contrast to the reaction with SCl_2, elemental sulfur is not formed as a byproduct.[4c] Preliminary attempts to prepare 1,5-$Cl_2P(NSN)_2PCl_2$ (**3**) from the reaction of $Cl_2P(NSiMe_3)N(SiMe_3)_2$ with either SCl_2 or $SOCl_2$ in dichloromethane or acetonitrile produced a mixture of phosphorus-containing products (^{31}P NMR) and, in the case of SCl_2, some elemental sulfur. Since the sulfur centers in 1,5-diphosphadithiatetrazocines are in the formal +3 oxidation state, we turned our attention to the use of a mixture of SCl_2 and SO_2Cl_2 in a 2:1 molar ratio as an in situ source of the "SCl_3" synthon.[29] As indicated in Scheme 2, the cyclocondensation of $Cl_2P(NSiMe_3)N(SiMe_3)_2$ with this sulfur(III) source produces 1,5-$Cl_2P(NSN)_2PCl_2$ (**3**) with elimination of trimethylchlorosilane provided that the solution of sulfur halides is added slowly to the phosphorus reagent. The product is isolated in 68% yield as an orange powder. However, when the same reaction is carried out with reverse addition of the reagents, the known six-membered ring $(Cl_2PN)_2(NSCl)$ is obtained in 90% yield.[30,31]

Scheme 2



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The identity of the eight-membered ring **3** was determined by electron-impact mass spectrometry in conjunction with elemental analyses. The EI mass spectrum of **3** exhibited a molecular ion peak at *m*/*z* = 323.7 with the characteristic pattern for a species with four Cl atoms, together with a peak at *m*/*z* = 277.8 corresponding to the loss of an NS fragment from the molecular ion. Although the parent ion appeared at *m*/*z* = 64 (S_2^+), there was no indication of the presence of *cyclo*-S_8, that is, a molecular ion at *m*/*z* 254 together with a series of ions corresponding to the sequential loss of sulfur atoms, in a freshly prepared sample of **3**. The elemental analyses (Cl, N, S) gave a Cl/N atomic ratio of 1.02:1 as required for the empirical formula Cl_2N_2PS. However, the high sulfur value indicated the presence of about 7% *cyclo*-S_8, possibly as a result of decomposition during transport of the analytical sample. The ^{31}P NMR spectrum of **3** exhibited a singlet at 93.7 ppm in CH_2Cl_2 or THF; no other resonances were apparent in the region +150 to −50 ppm, demonstrating that the sample was free of any phosphorus-containing impurities.

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(31) The six-membered ring $(Cl_2PN)_2(NSCl)$ was identified by NMR spectroscopy: δ ^{31}P (in d_8-THF), +24.8 (s) (cf. lit. + 24.5),[30,32] and EIMS (*m*/*z*): 278, 50%, $[M - Cl]^+$, 206, 39% $(M - 3Cl)^+$.

1,5-Diphosphadithiatetrazocines exhibit anomalously low-field isotropic solution ^{31}P NMR chemical shifts (+100 to + 140 ppm) compared to those of other unsaturated P−N−S rings, for example, 1,3-diphosphadithiatetrazocines, which typically lie in the region +30 to −21 ppm.[3b,4] These abnormal shifts persist in the solid state, and an analysis of the principle elements of the shielding tensor showed that one of these elements is primarily responsible.[6] Although the low-field shifts appear to be associated with the transannular S---S interaction in the 1,5-isomers, no correlation exists between this individual tensor component and the structural parameters of these folded eight-membered rings, for example, transannular S---S distance.

The heterocycle **3** exhibits thermochromic behavior in solution. At 303 K a CH_2Cl_2 solution is orange and the ^{31}P NMR singlet at 93.7 ppm has a half-width of 44 Hz. Upon cooling to 223 K the solution becomes pale yellow in color, and the half-width of the NMR resonance becomes narrower (20 Hz) without significant change in the chemical shift. Although the ^{31}P NMR chemical shift of **3** falls outside the range previously observed for 1,5-diphosphadithiatetrazocines, there is a consistent trend in the chemical shifts toward higher field as the substituents attached to phosphorus become more electronegative.[4b] The three structural isomers of **2**, all of which have electronegative CCl_3 and Cl substituents on each phosphorus atom, exhibit resonances in the range +100.5 to +113.8 ppm, and *d*(S---S) has been determined to be 2.525 Å for the *endo*, *endo* isomer.[4b] Thus, on the basis of the NMR data, it seems reasonable to infer that a transannular S---S interaction, possibly somewhat elongated, exists in **3**. Numerous attempts to confirm this feature by an X-ray structural determination were thwarted by facile decomposition in attempts to recrystallize **3** from organic solvents.

Physical Properties and Reactivity of 1,5-$Cl_2P(NSN)_2PCl_2$ (3). The tetrachloro derivative 1,5-$Cl_2P(NSN)_2PCl_2$ (**3**) is the first example of a 1,5-diphosphadithiatetrazocine in which both substituents on the phosphorus atoms are halogen atoms. The physical properties of **3** show significant differences from those of the corresponding tetraalkyl or tetraaryl derivatives 1,5-$R_2P(NSN)_2PR_2$ (R = Me, Et, Ph).[3,4] Whereas the latter are all white (or very pale yellow), air and thermally stable crystalline solids, the tetrachloro derivative **3** is an orange, extremely moisture-sensitive solid. In addition to a very strong absorption band at about 270 nm, compare 265 nm for 1,5-$Me_2P(NSN)_2PMe_2$ (**1**, R = Me),[3a] the UV−visible spectrum of a solution of **3** in CH_2Cl_2 exhibits a very weak band at about 445 nm, which presumably accounts for the orange color.

A characteristic reaction of chlorinated cyclophosphazenes $(Cl_2PN)_n$ is nucleophilic replacement of chlorine substituents using reagents such as secondary amines or alkoxides.[2] However, attempts to functionalize **3** at the phosphorus centers by reactions with nucleophiles, for example, aniline, diethylamine, methyl-lithium, or sodium phenoxide, all produced highly insoluble brown solids. It is possible that the known proclivity of 1,5-diphosphadithiatetrazocines to undergo nucleophilic attack at the sulfur centers[11,12] provides an alternative reaction pathway and, hence, a complex mixture of insoluble products is formed upon treatment of **3** with nucleophiles.

Thermolysis of 1,5-$Cl_2P(NSN)_2PCl_2$ (3). The tetrachloro derivative **3** is a potential precursor to the unknown inorganic polymer $[\text{-}Cl_2PSN\text{-}]_x$ containing alternating $[Cl_2PN]$ and S(III)N units in the backbone via ring-opening polymerization (ROP). A related P,N,S backbone polymer $[(NPCl_2)_2(NSCl)]_\infty$ composed of *two* $[Cl_2PN]$ groups and *one* [NS(IV)Cl] group in the repeating unit has been obtained by ROP of the homologous six-membered ring $(NPCl_2)_2(NSCl)$ at 90 °C.[32] The ring strain in the eight-membered ring **3** is expected to be lower than that in $(NPCl_2)_2(NSCl)$.

The thermolysis of a solution of **3** in C_6D_6 at 90−100 °C for 3 h resulted in only a small amount of decomposition as determined by ^{31}P NMR spectroscopy, which revealed several very weak resonances in the +6 to +25 ppm region in addition to the major resonance at 93.5 ppm for unchanged **3**. When solid samples of **3** were heated in a sealed tube under vacuum in the temperature range 80−120 °C the orange powder swelled slightly and became paler in color, but did not melt. By contrast to the observations for the solution decomposition, the ^{31}P NMR spectrum (in 1,4-dioxane) of the products of solid-state thermolysis at 100 °C for 1 h showed that **3** had completely decomposed to give the six-membered ring $(NPCl_2)_2(NSCl)$ (δ ^{31}P = 25.5 ppm) (via ring contraction) as the major product, together with numerous smaller resonances in the 0 to +18 ppm region. When the solid-state thermolysis was conducted for longer periods (3−16 h), the final product was an orange rubbery material, which is sparingly soluble in THF or dioxane, but more soluble in *N*,*N*-dimethylformamide (DMF). The ^{31}P NMR spectrum of a DMF solution revealed several resonances at −5 to +10 ppm; no traces of **3** were evident. Further attempts to characterize this intriguing rubber-like material were frustrated by partial decomposition with the elimination of elemental sulfur upon standing or on contact with organic solvents. In addition, we note that the identification of $(NPCl_2)_2(NSCl)$ as one of the initial thermolysis products suggests that the rubbery material may be contaminated with the polymer $[(NPCl_2)_2(NSCl)]_\infty$, which is known to be very moisture-sensitive.[32] A broad resonance observed at about −4 ppm for the decomposition products in DMF (cf. lit. value −4.6 ppm in dioxane for this polymer)[32] is consistent this suggestion.

Computational studies on 1,5-$R_2P(NSN)_2PR_2$. Computational studies have been carried out for the series 1,5-$R_2P(NSN)_2PR_2$ [**1a** (R = Me), **2** (R = Cl, R′ = CCl_3), **3** (R = Cl) and **4** (R = F)] to assess the influence of electronegative substituents on the structure of the eight-membered rings, and in an attempt to explain the unusual physical properties of **3**. For all four derivatives, the frontier orbitals show overlaps in both the S−S and N−N regions, which are also apparent in the electron density distributions (see Supporting Information). The S---S distance can be used as an indication of the strength of transannular S---S interaction in 1,5-diphosphadithiatetrazocines. The B3LYP computations predict that the

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Table 1. Key Atomic Distances (Å), NICS[a] (ppm), HOMO-LUMO gap(HLG, in eV), Vibrational Frequency of Symmetric Scissoring Mode (ν_{SS}, in cm^{-1}), and the Corresponding Vibrational Temperature (T_v(SS), in K) for 1,5-RR′P-(NSN)$_2$PRR′ Derivatives Predicted at the B3LYP/6-311+G(3df) Level[b]

	1a, R = Me, R′ = Me	**2**, R = Cl, R′ = CCl$_3$	**3**, R = Cl, R′ = Cl	**4**, R = F, R′ = F
S−N	1.595(1.595)	1.598(1.592)	1.599	1.598
P−N	1.621(1.636)	1.598(1.607)	1.599	1.582
S---S	2.621(2.551)	2.623(2.525)	2.629	2.669
NICS	−18.9	−17.5	−17.7	−16.1
δ_P	113.1	111.0(111.0)	102.8(93.7)	68.5
HLG	4.39	4.35	4.41	4.23
ν_{SS}	240	220	220	201
T_v(SS)	345	316	316	288

[a] NICS predicted by the GIAO method. [b] Experimental data are given in parentheses.

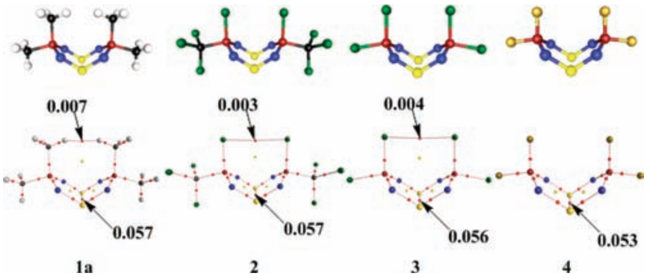

Figure 1. Geometries and QTAIM molecular graph (ρ(r) at BCP, unit: a.u.). Color scheme: black, C; white, H; blue, N, yellow, S; brown, P; green, Cl; gold, F; red, BCP.

transannular S---S distance becomes slightly elongated as the electronegativity of the substituents attached to the P atoms increases (viz. from 2.621 Å in **1a** (R = Me) to 2.669 Å in **4** (R = F) (Table 1). Thus the transannular S---S interaction is somewhat weaker in a 1,5-diphosphadithiatetrazocine with substituents of higher electronegativity. This trend is further corroborated by a QTAIM analysis; electron density ρ values at the S---S bond critical points (BCPs) follow the order of **1a** (0.057 au) = **2** (0.057 au) > **3** (0.056 au) > **4** (0.053 au) (Figure 1). Interestingly, additional BCP was also located between two hydrogen atoms or two chlorine atoms in **1a**, **2**, or **3**. However, their small ρ values (0.007, 0.003, and 0.004 au for **1a**, **2**, and **3**, respectively) demonstrate rather weak interactions.

Furthermore, it was demonstrated that 1,5-diphosphadithiatetrazocines are bishomoaromatic because of the transannular 6c-10e$^-$ through-space conjugation between the two (NSN)$^-$ subunits (Scheme 1). Table 1 shows the computed NICS values for **1a**, **2**, **3**, and **4**. All four derivatives are homoaromatic with negative NICS values (in the range of −16.1 to −18.9 ppm) at the geometric center of the homoconjugative (NSN)$_2$ segment of the eight-membered ring. It is interesting to note that the absolute NICS value decreases with increasing electronegativity of the substituents at P atoms, showing that the through-space homoconjugation is weaker in 1,5-diphosphadithiatetrazocines with substituents of higher electronegativity.

The GIAO-B3LYP/6-311+G(3df)-predicted ^{31}P NMR chemical shifts for the four 1,5-diphosphadithiatetrazocines **1a**−**4** are also listed in Table 1. The computed ^{31}P NMR chemical shift of **3** is high-field shifted by 8.2 ppm compared to that of **2**, in reasonable agreement with the experimental data (high-field shifted by 17.3 ppm). The ^{31}P NMR chemical shift of the hypothetical F-substituted congener **4** is 68.5 ppm, high-field shifted by 42.5 ppm compared to that of **2**.[33] Overall, the computations clearly predict the observed trend that the ^{31}P NMR chemical shift of 1,5-diphosphadithiatetrazocines is shifted to high field when the substituents attached to the P atoms are of higher electronegativity.

The fact that the ^{31}P NMR chemical shifts of 1,5-diphosphadithiatetrazocines are markedly low-field-shifted compared to those of other unsaturated monocyclic P−N−S rings, for example, 1,3-diphosphadithiatetrazocines (vide supra), can be attributed to the bishomoaromaticity of 1,5-diphosphadithiatetrazocines. In general, for a cyclic aromatic system, the cyclic electron current induced by an external magnetic field will result in a field-induced ring current that is magnetically shielding within the aromatic cycle, but deshielding out of the aromatic ring. Thus, the chemical shift of an atom located outside an aromatic ring will be downfield shifted compared to that of a non-aromatic system. In 1,5-diphosphadithiatetrazocines, the P atoms are outside the homoaromatic (NSN)$_2$ segment of the ring and, consequently, the ^{31}P NMR chemical shift should be shifted to low field because of the homoconjugation. Furthermore, the stronger the homoconjugation within the (NSN)$_2$ segment of the ring, the greater will be the chemical shift of the P atoms to low field in 1,5-diphosphadithiatetrazocines. This explains why the ^{31}P NMR chemical shift of **3** is high-field shifted compared to those of **1** and **2**, since the homoconjugation within **3** is weaker than that within **1** and **2**.

In addition, vibrational analyses of these compounds revealed that the scissoring mode, which can be regarded as the transannular S---S stretching mode, has a frequency in the range 200−240 cm^{-1}; the experimental value determined from the Raman spectrum of **1a** is 250 cm^{-1}.[3a] Moreover, the frequency decreases along with an increase in the electronegativity of the substituents on phosphorus. In the extreme case, the tetrafluoro derivative **4** has the lowest scissoring frequency (201 cm^{-1}) as well as the lowest corresponding vibrational temperature (288 K).[33] The predicted scissoring frequency is 220 cm^{-1} for **3** with a vibrational temperature of 316 K. Accordingly, there should be a large population of **3** at such a vibrational level at room temperature. This explains why the half-width of the NMR resonance of **3** in solution becomes narrower when temperature decreases from 303 to 223 K.

Finally, we note that the UV−visible spectra of **1a** (R = Me)[3a] and **3** exhibit a strong absorption band in the region 265−270 nm, which can be ascribed to the HOMO→LUMO transition. In agreement with the UV−vis spectra, TD-B3LYP/6-311+G(3df) computations[34] showed that

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(33) In previous investigations of unsaturated P-N-S rings we found that the replacement of aryl or alkyl substituents on phosphorus by fluorine resulted in a much lower stability. In the case of six-membered rings (R$_2$PN)(SN)$_2$, which are lower homologues of **1** and **4**, the difluoro derivative (R = F) is a thermally unstable blue oil. See: (a) Burford, N.; Chivers, T.; Cordes, A. W.; Laidlaw, W. G.; Noble, M. C.; Oakley, R. T.; Swepston, P. N. *J. Am. Chem. Soc.* **1982**, *104*, 1282. (b) Burford, N.; Chivers, T.; Oakley, R. T.; Oswald, T. *Can. J. Chem.* **1984**, *62*, 712.

(34) For time-dependent (TD) density functional theory, see: Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454.

the HOMO→LUMO transition occurs with high absorption intensity at about 4.41 eV (ca. 281 nm) for **3** and about 4.43 eV (ca. 279 nm) for **1a**. The origin of the *very weak* absorption band at about 445 nm in the visible spectrum of **3** is not apparent from the calculations.

Conclusions

A cyclocondensation method has been developed for the successful synthesis of 1,5-$Cl_2P(NSN)_2PCl_2$ (**3**), the first example of a tetrahalogenated derivative of an unsaturated $P_2N_4S_2$ ring. The low-field ^{31}P NMR chemical shift of **3** is strongly indicative of a bicyclic structure with a transannular S---S contact, and this interaction is further predicted by DFT computations. The computational results also show that 1,5-diphosphadithiatetrazocines exhibit bishomoaromatic character because of through-space homoconjugation between the two $(NSN)^-$ subunits. This conjugation is weakened with an increase of the electronegativity of the substituents and accounts for the low-field ^{31}P NMR chemical shifts of these folded eight-membered rings, which are shifted to high field when the substituents attached to the P atoms are of higher electronegativity.

The physical properties of **3** are in marked contrast to those of tetra-alkyl or -aryl derivatives. Specifically, the orange color and thermal lability are distinctive features of **3**. The latter characteristic provides a source of an intriguing rubber-like material, but this transformation is accompanied by ring contraction and the partial loss of sulfur which precludes a definitive characterization.

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Supporting Information Available: The frontier orbitals and electron densities of **1a**−**4** (Figure S1), selected molecular orbitals for the 6c−10e homoconjugation in **3** (Figure S2), and a Table of the Cartesian coordinates and total electronic energies for compounds **1a**−**4** (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.