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

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The first example of a tetrahalogenated derivative of a diphosphadithiatetrazocine, 1,5-Cl₂P(NSN)₂PR₂ (3), was synthesized by cyclocondensation of a 2:1 mixture of SCl₂ and SO₂Cl₂ with Cl₂P(NSiMe₃)₂N(SiMe₃)₂ in CH₂Cl₂. The heterocycle 3 was isolated as an orange, moisture-sensitive, thermally labile solid and characterized by mass spectrometry, ³¹P NMR, and UV-visible spectroscopy. The low-field ³¹P NMR chemical shift (93.7 ppm) is indicative of a cross-ring S—S interaction in the eight-membered P₂N₄S₂ 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-R₂P(NSN)₂PR₂ (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 R₂P(NSN)₂PR₂ are eight-membered rings that may be considered as hybrids of the well-known cage molecule S₄N₄¹ and monocyclic cyclotetraphosphazenes (R₂P)₄.² The isomer 1,5-Me₂P(NSN)₂PMe₂ was first obtained in 1982 via decomposition of the six-membered ring (Me₂PN)(SN)₂, which was prepared by the reaction of S₄N₄ with Me₂PPh₂.³ Subsequently, improved syntheses for a variety of derivatives of the type 1,5-R₂P(NSN)₂PR₂ (I, 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-S₈) 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)₂PR' (R = Me, R' = Ph; R = Cl, R' = CCl₃), 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

1,5-Diphosphadithiatetrazocines serve as excellent models for elucidating the initial outcome of reactions of sulfur–nitrogen compounds. The folded rings 1 exhibit ³¹P NMR...
chemical shifts at anomalously low fields (100–140 ppm), compared to those of cyclophosphazenes, both in the solid state and in solution. 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 S₄N₄ cage, 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 and with platinum(II), the S--S contact is maintained in these adducts. The oxidative addition of halogenos to 1 (R = Ph) produces the exo, endo dihalogenated derivatives 1,5-R₃P-(NS(X)N)PR₂ (X = Cl, Br). The latter have been used as a source of the diacids [Et₂P(NSN)₂P₂Et₂]₄, which is a planar eight-membered ring. The P₂N₄S₂ ring in 1 is also readily susceptible to nucleophilic attack at sulfur; reactions with organolithium reagents produce the dimeric adducts [Li{(Ph₂P)₂N₂S₂R}]. Alkali-metal derivatives of the dianion [Ph₂P₂N₄S₂]⁻ may also be prepared by the reaction of 1 (R = Ph) with M[Et₃BH]. The combination of hard (S) and soft (S) coordination sites confers 1 with a versatile coordination chemistry. The formation of η²-S,S' complexes with platinum are of particular interest in view of a bonding analogy with η²-alkene complexes.

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. Early approximate density functional theory (DFT) calculations for 1,5-Me₂P(NSN)₂PMe₂ estimated the S--S bond energy to be 133 kJ mol⁻¹, and a subsequent DFT calculation at the B3LYP level for the model system 1,5-H₂P(NSN)₂PH₂ concluded that the bond order is about 0.7. 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 (homojunction) 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). An alternative description of 1 as trishomoaromatic molecules has subsequently been suggested.

In the context of the current interest in the unsaturated, bicyclic P₃N₄S₂ system, we report the synthesis of 1,5-Cl₃P-(NSN)₂PCl₂ (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 (Cl₃P(NSN))₄ via ring-opening polymerization was an intriguing possibility, since this putative PNSN backbone polymer is a hybrid of the well-known inorganic polymers [Cl₃P(NP)]₄ and [SN]₆, which are elastomeric and conducting materials, respectively. Complementary quantum chemistry computations have been carried out for 3, as well as the unknown fluorine analogues 1,5-F₃P(NSN)₂PF₃ (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 Cl₅P(NSiMe₃)₂-N(SiMe₃)₂ was prepared by the published procedure. The reagents Cl₃S and SO₂Cl₂ were obtained from Aldrich. Cl₅S was purified by vacuum distillation (ca. 1 Torr) from PCl₃ and then used immediately to minimize disproportionation into S₄Cl₂ and Cl₂SO₂Cl₂ 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 CH₂Cl₂ 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-Cl₃P(NSN)₂PCl₂ (3).** A golden yellow solution of a mixture of Cl₅S (0.812 g, 7.89 mmol) and SO₂Cl₂ (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 Cl₅P-(NSiMe₃)₂N(SiMe₃)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 [NPMe₃] and [NSi(O)]₈ 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.
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-Cl2P(NSiMe3)PCl2 (3) (0.883 g, 2.73 mmol, 68%) as a free-flowing orange powder. 31P 1H NMR (CD2Cl2, 23 °C): δ 93.7 (s). EIMS (70 eV): m/z 323.7 (M+, 42%), 277.8 ([M − SN]1), 8%, 64.1 (S2, 100%), UV−vis (CD2Cl2, nm): λmax 270 (s), 445 (vw). Anal. Calcld for Cl2N2PS: Cl, 43.78; N, 17.30; S, 24.8 (s) (cf. lit. 24.5), 30,32 and EIMS (m/z): 278, 50%, [M + Cl]+, 206, 39% ([M − 3Cl]−).

**Thermalolysis of 1,5-Cl2P(NS2)2PCl2 (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 31P NMR spectroscopy. The details of these spectra are discussed 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.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.20

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-Cl2P(NSN)2PCl2 (3).** 1,5-Diphosphadithiatetrazocines are best prepared by cyclocondensation reactions of the readily available reagents R2P(NSiMe3)2N(SiMe3)2 (R = allyl, aryl) or the lithium reagent Li[P3H2(PNSiMe3)2] with

(SCl2 or SOCl2,2,3,4) The ligand reagent gives higher yields, and the products are more easily purified since, in contrast to the reaction with SCl2, elemental sulfur is not formed as a byproduct.26 Preliminary attempts to prepare 1,5-Cl2P(NS2)2PCl2 (3) from the reaction of Cl2P(NSiMe3)2N(SiMe3)2 with either SCl2 or SOCl2 in dichloromethane or acetonitrile produced a mixture of phosphorus-containing products (31P NMR) and, in the case of SCl2, 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 SCl2 and SOCl2 in a 2:1 molar ratio as an in situ source of the “SCl2” synthon.29 As indicated in Scheme 2, the cyclocondensation of Cl2P(NSiMe3)2N(SiMe3)2 with this sulfur(III) source produces 1,5-Cl2P(NSN)2PCl2 (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 (Cl2PN)2(NSCl) is obtained in 90% yield.30,31

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 (S2), there was no indication of the presence of cyclo-S8, 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 Cl2N2PS. However, the high sulfur value indicated the presence of about 7% cyclo-S8, possibly as a result of decomposition during transport of the analytical sample. The 31P NMR spectrum of 3 exhibited a singlet at 93.7 ppm in CH2Cl2 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.

(29) A mixture of SeCl2 and SCl2 in a 4:1 molar ratio was used to generate “SeCl2” for the synthesis of the selenium analogues 1,5-R2P(NSSeN)2PR3 (R = Me, Ph). See: Chivers, T.; Doxsee, D. D.; Parvez, M. Inorg. Chem. 1993, 32, 2238.

(30) The same-membered ring (Cl3PN)2(NSCl) was identified by NMR spectroscopy: δ 31P (in d6-THF), +24.8 (s) (cf. lit. +24.5),30,32 and EIMS (m/z): 278, 50%, [M − Cl]−, 206, 39% ([M − 3Cl]−).

(31) The same-membered ring (Cl2PN)2(ScI) was identified by NMR spectroscopy: δ 31P (in d6-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 $^{31}$P NMR chemical shifts (100 to $-140$ ppm) compared to those of other unsaturated $P-N-S$ rings, for example, 1,3-diphospha-

The heterocycle $\mathbf{3}$ exhibits thermochromic behavior in solution. At 303 K a CH$_2$Cl$_2$ 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 $\mathbf{3}$ falls outside the range previously observed for 1,5-

The three structural isomers of $\mathbf{2}$, all of which have electronegative CCl$_3$ and C 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.\textsuperscript{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 $\mathbf{3}$. Numerous attempts to confirm this feature by an X-ray structural determination were thwarted by facile decomposition in attempts to recrystallize $\mathbf{3}$ from organic solvents.

Physical Properties and Reactivity of 1,5-Cl$_2$P(NSN)$_2$PCl$_2$ (3). The tetrachloro derivative 1,5-Cl$_2$P(NSN)$_2$PCl$_2$ (3) is the first example of a 1,5-diphosphadithiatetrazocene in which both substituents on the phosphorus atoms are halogen atoms. The physical properties of $\mathbf{3}$ show significant differences from those of the corresponding tetraalkyl or tetraaryl derivatives 1,5-R$_2$P(NSN)$_2$PR$_2$ (R = Me, Et, Ph).\textsuperscript{3,4} Whereas the latter are all white (or very pale yellow), air and thermally stable crystalline solids, the tetrachloro derivative $\mathbf{3}$ is an orange, extremely moisture-sensitive solid. In addition to a very strong absorption band at about 270 nm, compare 265 nm for $\mathbf{1}$, the UV–visible spectrum of a solution of $\mathbf{3}$ in CH$_2$Cl$_2$ exhibits a very weak band at about 445 nm, which presumably accounts for the orange color.

A characteristic reaction of chlorinated cyclophosphazenes (Cl$_2$PN)$_n$ is nucleophilic replacement of chlorine substituents using reagents such as secondary amines or alkoxides.\textsuperscript{5} However, attempts to functionalize $\mathbf{3}$ 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-

The thermolysis of a solution of $\mathbf{3}$ in C$_6$D$_6$ 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 $\mathbf{3}$. When solid samples of $\mathbf{3}$ 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 $\mathbf{3}$ had completely decomposed to give the six-membered ring (NPCl$_2$)(NSCl) ($\delta$ $^{31}$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 $\mathbf{3}$ 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$_2$)(NSCl) as one of the initial thermolysis products suggests that the rubbery material may be contaminated with the polymer (NPCl$_2$)(NSCl)$_n$ which is known to be very moisture-sensitive.\textsuperscript{2} 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)\textsuperscript{32} is consistent this suggestion.

Computational studies on 1,5-R$_2$P(NSN)$_2$PR$_2$. Computational studies have been carried out for the series 1,5-R$_2$P(NSN)$_2$PR$_2$ (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 $\mathbf{3}$. 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


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 31P NMR chemical shifts for the four 1,5-diphosphadithiatetrazocines 1a–4 are also listed in Table 1. The computed 31P 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 31P 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. Overall, the computations clearly predict the observed trend that the 31P 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 31P 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 31P 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 31P 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. 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). 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−vis absorbance of 1a (R = Me) 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 showed that (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,P,N)(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.; Sweeplstow, P. N. J. Am. Chem. Soc. 1982, 104, 1292. (b) Burford, N.; Chivers, T.; Oakley, R. T.; Oswald, T. Can. J. Chem. 1984, 62, 712.

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-Cl₂P(NSN)₂PCl₂ (3), the first example of a tetrahalogenerated derivative of an unsaturated P₂N₄S₂ ring. The low-field ³¹P NMR chemical shift of 3 is strongly indicative of a bicyclic structure with a trans-annular 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 ³¹P 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.