^1H NMR (obtained from benzene-d_6 solution at +16 °C relative to Me_4Si) δ 1.43 (s, 18 H), 7.20 (m, 10 H).

IR 2917 s, 1575 m, 1465 s, 1368 s, 1310 s, 1260 m, 1232 w, 1170 s, 1027 m, 945 s, 785 m, 760 s, 688 s, 670 w, 570 m, 520 w, 465 m cm^{-1}.

In the mass spectrum, the ion of highest mass corresponded to $Mo(O\text{-}t\text{-}Bu)_2(NC_6H_5)_2^+$ at m/e 426 based on ^{98}Mo.

A reaction involving $C_6H_5{}^{15}N^{14}N_2$ gave $Mo(O\text{-}t\text{-}Bu)_2(^{15}NC_6H_5)_2^+$ at m/e 428 based on ^{98}Mo. The IR spectrum showed a shift of the band at 1310 cm^{-1} to 1280 cm^{-1}, assignable to $\nu(Mo\text{-}^{14}N)$ and $\nu(Mo\text{-}^{15}N)$, respectively.

$[Mo(O\text{-}t\text{-}Bu)_2(NC_7H_7)_2]_2$, where C_7H_7 = *p*-tolyl, was prepared similarly as a yellow crystalline solid, appreciably soluble in hexane, benzene, and toluene. In the mass spectrometer, the ion of highest mass corresponded to $Mo(O\text{-}t\text{-}Bu)_2(NC_7H_7)_2^+$ at m/e 454. ^1H NMR (obtained from toluene-d_8 at +16 °C relative to Me_4Si) δ 1.47 (s, 18 H), 2.06 (s, 6 H), 6.80 (d, 4 H); 7.31 (d, 4 H); IR 2900 s, 1490 m, 1460 s, 1370 s, 1292 w, 1258 s, 1230 w, 1155 s, 1111 w, 1098 w, 1004 w, 950 s, 915 w, 895 s, 808 s, 780 m, 712 w, 524 w cm^{-1}.

X-ray Structural Determination of $[Mo(O\text{-}t\text{-}Bu)_2(NC_7H_7)_2]_2$. General operating procedures and computational techniques have been described previously.[15]

A crystal of dimensions 0.24 × 0.26 × 0.28 mm was mounted in a nitrogen-filled glovebag and transferred to the liquid nitrogen boil-off cold stream of the diffractometer. The cell dimensions, determined from 44 reflections by using Mo Kα radiation, λ = 0.71069 Å, at -170 °C were a = 10.789 (2) Å, b = 25.904 (6) Å, c = 13.007 (3) Å, α = 73.11 (1)°, β = 81.34 (1)°, γ = 91.25 (1)°; V = 3430.3 (1) Å^3, Z = 3, d_{calcd} = 1.314 g cm^{-3}, and space group $P\bar{1}$.

A total of 9734 reflections were collected, including redundancies, and were reduced to 8946 unique reflections by using standard moving-crystal, moving-detector techniques, with the following values: scan speed = 6.0°/min, scan width = 1.7 + dispersion, single background at extreme of scan = 3 s, aperture size = 3.0 × 4.0 mm. The limits of data collection were 6° < 2θ < 45°. The number of reflections with $F > 2.33\sigma(R)$ was 7701. Since the crystal was nearly equidimensional, no absorption correction was attempted (μ(Mo Kα) = 5.76 cm^{-1}).

The structure was solved by a combination of direct methods and Fourier techniques. All nonhydrogen atoms were located and refined with anisotropic thermal parameters. The refinement was carried out in a cyclic manner due to the large number of parameters. Becuase of the size of the problem, no attempt was made to locate hydrogen atoms. The final residuals are R_F = 0.076 and R_{wF} = 0.086. The goodness of fit for the last cycle was 2.127 and the maximum σ/Δ was 0.05.

The rather large residuals and goodness of fit are partically due to the large thermal motion observed in several of the *tert*-butoxy ligands. A careful examination of a final difference Fourier synthesis did not reveal any apparent disorder and was essentially featureless.

Acknowledgment. We thank the National Science Foundation for financial support and the Marshal H. Wrubel Computing Center for computing facilities. M.H.C. is grateful for a NATO grant with Professor D. C. Bradley, Queen Mary College, London.

Registry No. $[Mo(O\text{-}t\text{-}Bu)_2(NPh)_2]_2$, 78134-34-6; $[Mo(O\text{-}t\text{-}Bu)_2(NC_7H_7)_2]_2$, 78134-33-5; $Mo_2(O\text{-}t\text{-}Bu)_6$, 60764-63-8; phenyl azide, 622-37-7; *p*-tolyl azide, 2101-86-2.

Supplementary Material Available: Listing of observed and calculated structure factors (56 pages). Ordering information is given on any current masthead page.

(15) Caulton, K. G.; Huffman, J. C.; Lewis, L. N. *Inorg. Chem.* **1980**, *19*, 2755.

Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

Preparation and Crystal, Molecular, and Electronic Structure of 1,1,5,5-Tetramethylbicyclo[3.3.0]-1,5-diphospha-3,7-dithia-2,4,6,8-tetrazene: A Bicyclic PSN System with a Sulfur-Sulfur Bond

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1,1-Dimethyl-1-phospha-3,5-dithia-2,4,6-triazene, $Me_2PS_2N_3$, prepared by the reaction of Me_2PPMe_2 with S_4N_4, undergoes a ring expansion at ambient temperature to give 1,1,5,5-tetramethylbicyclo[3.3.0]-1,5-diphospha-3,7-dithia-2,4,6,8-tetrazene, $Me_2P(NSN)_2PMe_2$, whose crystal and molecular structure has been determined by single-crystal X-ray diffraction. The crystals of $Me_2P(NSN)_2PMe_2$ are orthorhombic, space group *Pnma*, with a = 11.081 (5) Å, b = 8.216 (5) Å, c = 11.837 (6) Å, V = 1077.7 Å^3, Z = 4, and D_c = 1.49 g cm^{-3}. The structure was solved by direct methods and refined anisotropically to a final conventional R factor of 0.033 for 692 reflections with $I > 3\sigma(I)$. The structure consists of a folded eight-membered ring (butterfly) with a cross-ring S-S contact of 2.551 (2) Å. The angle between the two intersecting planes of the eight-membered ring is 114.9 (2)°. The mean endocyclic P-N and S-N bond lengths are 1.636 (3) and 1.595 (3) Å, respectively. The ^1H and ^{13}C NMR spectra of $Me_2P(NSN)_2PMe_2$ are consistent with nonequivalent pairs of methyl groups, suggesting that the folded structure is maintained in solution. Simple Hückel calculations have been carried out for eight-membered ring systems of the type $E(NSN)_2E$ that lead to the prediction that a planar structure will be favored over a structure folded about a transannular S-S bond for the more electronegative substituents, E.

Introduction

We have recently extended our studies of the reactions of phosphines with S_4N_4[1] to the diphosphines R_2PPR_2 (R = Ph,[2] Me[3]). The products of these reactions, $R_2PS_2N_3$, are six-membered 8-π-electron ring systems whose intense color (R = Ph, λ_{max} = 550 nm; R = Me, λ_{max} = 543 nm) is attributed to a low-energy $\pi^* \rightarrow \pi^*$ electronic transition.[2,3] The dimethyl derivative, a purple oil, decomposes at room temperature to give a yellow crystalline solid, identified in this study as an eight-membered bicyclic ring. We discuss here the formation and spectroscopic and X-ray structural characterization of this

(1) (a) Bojes, J.; Chivers, T.; Maclean, G.; Oakley, R. T.; Cordes, A. W. *Can. J. Chem.* **1979**, *57*, 3191. (b) Bojes, J.; Chivers, T.; Cordes, A. W.; Oakley, R. T.; Maclean, G. *Inorg. Chem.* **1981**, *20*, 16.
(2) Burford, N.; Chivers, T.; Oakley, R. T.; Cordes, A. W.; Swepston, P. N. *J. Chem. Soc., Chem. Commun.* **1980**, 1204.
(3) Burford, N.; Chivers, T.; Laidlaw, W. G.; Oakley, R. T.; Cordes, A. W.; Pennington, W. T.; Swepston, P. N. *J. Am. Chem. Soc.*, in press.

new PNS system. We also compare the structure and bonding in this compound with that of related eight-membered rings of the type $E(NSN)_2E$ and, on the basis of simple Hückel MO calculations, predict the effect of changing the electronegativity of the substituents E on the conformation of the ring.

Experimental Section

Reagents and General Procedures. Tetrasulfur tetranitride[4] and tetramethyldiphosphine[5] were prepared by the literature methods. Tetramethyldiphosphine disulfide (Strem) and iron powder (Ventron) were commercial products used as received. All the solvents employed were of reagent grade and were dried before use: toluene by distillation from sodium, acetonitrile by double distillation from P_2O_5 and calcium hydride, and dichloromethane by distillation from P_2O_5. Anhydrous diethyl ether (Mallinckrodt) was used as received. All distillations of solvents and all reactions were carried out under an atmosphere of nitrogen (99.99% purity) passed through Ridox and silica gel. Infrared spectra (4000–250 cm^{-1}) were recorded as Nujol mulls (CsI windows) on a Perkin-Elmer 467 grating spectrophotometer. UV–visible spectra were obtained with a Cary 15 spectrophotometer. ^1H, ^{31}P, and ^{13}C NMR spectra were obtained on a Varian XL 200-MHz spectrometer. Raman spectra were recorded on samples in glass capillaries with a Jarrel-Ash Model 25-100 double-grating spectrometer with a photon-counting detection system, with use of a Coherent Radiation dye laser pumped by a CR-4 argon ion laser. Mass spectra were recorded on a Varian CH5 instrument operating at 70 eV. Chemical analyses were performed by M.H.W. Laboratories, Phoenix, AZ.

Formation of $Me_2P(NSN)_2PMe_2$ from $Me_2PS_2N_3$. Pure $Me_2PS_2N_3$ (0.18 g, 1.1 mmol), prepared from tetrasulfur tetranitride and tetramethyldiphosphine in toluene at reflux,[3] was left in a sealed flask at 23 °C under nitrogen for 7 days. A ^{31}P NMR spectrum of the reaction mixture in $CDCl_3$ revealed the presence of a major product (identified below as $Me_2P(NSN)_2PMe_2$) at $\delta = -77.7$ (reference external 85% H_3PO_4), $(Me_2PN)_3$ ($\delta = 25.8$), and minor amounts of $(Me_2PN)_4$ ($\delta = 19.3$). S_4N_4 was isolated from the mixture along with a toluene-insoluble pale yellow solid which was recrystallized from methylene chloride–acetonitrile to give yellow diamond-like crystals of $Me_2P(NSN)_2PMe_2$ (0.08 g, 0.33 mmol, 40% yield based on N; dec 175–180 °C). Anal. Calcd for $C_4H_{12}N_4P_2S_2$: C, 19.83; H, 4.99; N, 23.13; P, 25.57; S, 26.47. Found: C, 19.98; H, 4.69; N, 22.91; P, 25.44; S, 26.39. The infrared spectrum of $Me_2P(NSN)_2PMe_2$ (1600–250-cm^{-1} region) shows bands at 1402 vw, 1292 s, 1287 w, 1112 s, 1050 vs, 955 s, 887 m, 871 w, 796 vw, 753 w, 723 vw, 688 s, 663 w, 647 s, 512 vw, 504 vw, 450 m, 426 w, and 359 vw cm^{-1}. The UV–visible spectrum (in CH_2Cl_2) shows one band at 265 nm ($\epsilon \sim 10^3$ L mol^{-1} cm^{-1}). A parent ion peak was observed at m/e 242 in the mass spectrum. The phosphorus-decoupled ^1H NMR spectrum of $Me_2P(NSN)_2PMe_2$ in $CDCl_3$ showed singlets at δ 1.46 and 1.51; the ^{13}C NMR spectrum showed doublets at δ 19.6 ($^1J_{C-P} = 92$ Hz) and δ 18.9 ($^1J_{C-P} = 75$ Hz); the ^{31}P NMR spectrum showed a singlet at δ −77 (reference external 85% H_3PO_4). All NMR spectra were recorded in $CDCl_3$ solution.

X-ray Data Collection. The crystal data and experimental conditions are given in Table I. A diamond-shaped crystal was glued at its sharpest point onto a glass fiber. Preliminary photographic examination and observed extinctions during data collection, $(hk0)$, $h = 2n + 1$, $(0kl)$, $k + l = 2n + 1$, identified the space group as either *Pnma* or $Pn2_1a$. *Pnma* was the final choice on the basis of the centric distribution of E values.

All the data were collected on an Enraf-Nonius CAD4 automated diffractometer fitted with a low-temperature attachment. The cell constants and orientation matrix were determined by least-squares refinement of the diffraction geometry for 16 reflections having 11° $\leq \theta \leq$ 14°. The ω scan was collected in 96 steps; of these the first 16 and last 16 steps were considered to be background. The intensity was calculated as $I = [P - 2(B1 + B2)]Q$, where P is the sum of the central 64 steps, Q is the scan rate, and $B1$ and $B2$ are the backgrounds.

Table I. Crystal Data

$C_4H_{12}N_4P_2S_2$	$c = 11.837$ (6) Å
crystal system: orthorhombic	$V = 1078$ (1) Å^3
space group: *Pnma*	$Z = 4$
$a = 11.081$ (5) Å	mol wt = 242.24
$b = 8.216$ (5) Å	$D_c = 1.49$ g cm^{-3}

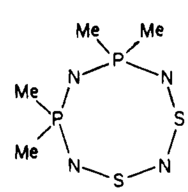
radiation: Mo Kα (graphite monochromator), $\lambda = 0.710\,69$ Å
max θ: 30°
scan type: ω–2θ
scan speed: 0.4–6.7° min^{-1} to give $I/\sigma(I) \geq 2.5$ to a maximum time of 120 s/rflctn
scan range: $\Delta\omega = 1.5(0.6 + 0.347 \tan\theta)$°
std rflctns: $(\bar{1}26)$, $(4\bar{3}3)$, and $(\bar{7}02)$; remeasured every 1000 s of X-ray exposure time and showed no significant intensity fluctuation
temp: −100 (5) °C
rflctns: 1818 unique rflctns, of these 692 had $I > 3\sigma(I)$
absorption coefficient: μ(Mo Kα) = 7.309 cm^{-1}
cryst dimensions: ca. 0.22 × 0.25 × 0.27 mm
boundary planes: $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1})$, (001), (110), $(\bar{1}\bar{1}0)$, (111), $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}\bar{1}1)$, $(11\bar{1})$

The standard deviation of the intensity $\sigma(I) = [P + 4(B1 + B2)]^{1/2}Q$. Lorentz and polarization corrections were applied, and E values were calculated by using a K curve.

Solution and Refinement. Initial coordinates for the two phosphorus atoms, three of the four carbon atoms, two unique nitrogen atoms, and one unique sulfur atom were obtained by direct methods (MULTAN 78). After correction of the scale, the initial coordinates for the fourth carbon atom were obtained from a difference Fourier synthesis. A further two cycles of isotropic refinement resulted in an agreement factor of $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.047$. A difference Fourier synthesis, following three anisotropic refinement cycles, revealed the positions of the eight unique hydrogen atoms, which were included in the model with the thermal parameters of the carbon atom to which they are attached but were not refined. Subsequent anisotropic refinement of the nonhydrogen atoms resulted in a final agreement factor of $R = 0.033$. On the final cycle the maximum shift/error was 0.01 and the standard deviation of an observation of unit weight was 2.76.

Results and Discussion

Preparation and Spectroscopic Characterization of $Me_2P(NSN)_2PMe_2$. The thermal stability of phosphadithiatriazenes, $R_2PS_2N_3$, is markedly dependent on the nature of the substituents R. When R = Ph[2] or Me_3SiNH[6] the compound is a crystalline solid and the phenyl derivative is stable for at least 24 h at reflux in mesitylene. By contrast, when R = Me the compound is an unstable, volatile, purple oil (mp 16–17 °C) which decomposes at room temperature under nitrogen to give S_4N_4, $(Me_2PN)_3$, $(Me_2PN)_4$, and a yellow crystalline solid. Complete elemental analysis of the yellow product reveals the empirical formula $(CH_3)_2PN_2S$, and the mass spectral data (parent ion at m/e 242) suggest that the compound is the dimer of this formula unit. The most likely structural alternatives appear to be an eight-membered ring in which the phosphorus atoms are in either the 1,3- or the 1,5-positions (**1** or **2**).



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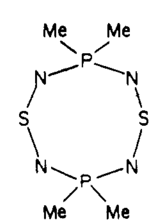

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The ^{31}P NMR spectrum exhibits a singlet, indicating equivalent phosphorus atoms. The $^1H\{^{31}P\}$ NMR spectrum, which consists of two singlets, and the ^{13}C NMR spectrum,

(4) Villena-Blanco, M.; Jolly, W. L. *Inorg. Synth.* **1967**, *9*, 98.
(5) Butter, S. A.; Chatt, J. *Inorg. Synth.* **1974**, *15*, 187. In our hands the reaction of tetramethyldiphosphine disulfide with *an excess* of iron produced a mixture of trimethylphosphine and tetramethyldiphosphine. The former reacts with S_4N_4 to give Me_3PS, which is difficult to separate from $Me_2PS_2N_3$. When a *stoichiometric* quantity of iron was used, the Me_2PPMe_2 obtained was not contaminated with Me_3P.
(6) Appel, R.; Halstenberg, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 696.

Table II. S-S Bond Lengths and Raman Stretching Frequencies in Sulfur-Nitrogen Cages and Bicyclic Compounds

S-N cage or bicyclic	d(S-S), Å	ν(S-S), cm^{-1}
$Me_2NC(NSN)_2CNMe_2$	2.43[a]	
S_5N_6	2.43[b]	269[b]
1,5-$(Ph_3P{=}N)_2S_4N_4$	2.45[c]	259[d]
1,5-$Cl_2S_4N_4$	2.48[e]	260[d]
$Me_2P(NSN)_2PMe_2$	2.55[f]	250[f]
S_4N_4	2.58[g]	213[h,j]
$S_4N_5^-$	2.71[i]	186[d]
$S_4N_5O^-$	2.63[j]	222[j]

[a] Reference 9. [b] Reference 8. [c] Reference 1. [d] Chivers, T.; Lau, C.; R. T. Oakley, R. T., unpublished data. [e] Reference 10. [f] This work. [g] Reference 11. [h] Reference 12. [i] Reference 13. [j] Steudel, R. *Z. Naturforsch., A* **1981**, *36A*, 850. This assignment has been confirmed by measurement of the Raman spectrum of $S_4{}^{15}N_4$.

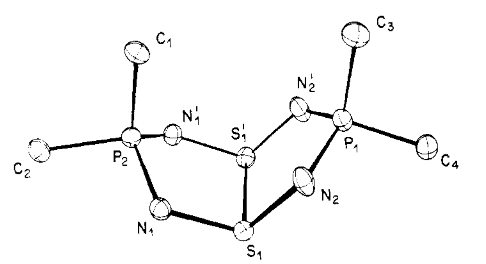
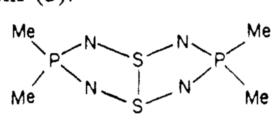


Figure 1. ORTEP plot (50% probability ellipsoids) for $Me_2P(NSN)_2PMe_2$ showing the atomic numbering scheme.

which shows two doublets, suggest inequivalent pairs of methyl groups. Thus the NMR data do not unequivocally distinguish between the 1,3 and 1,5 isomers but do rule out a planar configuration for the eight-membered ring.[7]

Further structural information comes from the Raman spectrum, which shows a strong band at 250 cm^{-1}. The observation of a strong Raman band at ca. 269 cm^{-1} in S_5N_6 has been tentatively assigned to the transannular S–S bond.[8] The fact that a similar band whose frequency is dependent on S–S bond length is observed in the Raman spectra of related sulfur–nitrogen cages and bicyclic compounds (see Table II) provides strong support for this assignment and, in the present case, suggests that the structure is an eight-membered ring folded about a cross-ring S–S bond with phosphorus atoms in the 1,5-positions (**3**).



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In order to confirm this proposal, an X-ray structural determination has been carried out. The details are described below.

Crystal and Molecular Structure of $Me_2P(NSN)_2PMe_2$. As indicated in Figure 1, the X-ray structural determination confirms the spectroscopic assignment of an eight-membered ring with a significant S–S cross-ring bonding interaction. Table III lists the atomic coordinates for the unique portion (C_2P–NSN–PC_2) of the molecule, which is positioned on a crystallographic mirror plane containing the two phosphorus atoms and all four carbon atoms. Thermal parameters, parameters for the hydrogen atoms, and a list of structure factors are available as Supplementary Material. The bond lengths and bond angles for the nonhydrogen atoms are summarized in Table IV.

By analogy with the related molecules 1,5-$(Ph_3P{=}N)_2S_4N_4$[1] and $Me_2NC(NSN)_2CNMe_2$,[9] $Me_2P(NSN)_2PMe_2$ can be viewed as a bicyclic molecule in which two five-membered rings share a common S–S bond. As a result of the crystal-

Table III. Atomic Coordinates of the Asymmetric Unit C_2P-NSN-PC_2 ($\times 10^4$) with Esd's in Parentheses

atom	x/a	y/b	z/c
P1	4195 (1)	7500[a]	0310 (1)
P2	0538 (1)	7500[a]	0469 (1)
N1	1080 (3)	9110 (4)	1115 (2)
N2	3469 (3)	9125 (4)	0713 (3)
S1	2411 (1)	9052 (1)	1627 (1)
C1	0817 (5)	7500[a]	−1026 (4)
C2	−1069 (5)	7500[a]	0647 (4)
C3	4420 (5)	7500[a]	−1192 (5)
C4	0685 (5)	7500[a]	4104 (5)

[a] Parameters are restricted by the symmetry of the crystal.

Table IV. Selected Bond Lengths (Å) and Angles (Deg) with Esd's in Parentheses for $Me_2P(NSN)_2PMe_2$

P1-N2	1.630 (3)	P2-C2	1.792 (5)
P2-N1	1.642 (3)	N1-S1	1.594 (3)
P1-C3	1.795 (6)	N2-S1	1.597 (3)
P1-C4	1.790 (6)	S1-S1'	2.551 (2)
P2-C1	1.797 (5)		
N2'-P1-N2	110.0 (2)	C2-P2-N1	108.0 (1)
N1'-P2-N1	107.3 (2)	N1-S1-N2	114.9 (2)
C3-P1-C4	104.8 (3)	N1-S1-S1'	91.7 (1)
C3-P1-N2	111.0 (2)	N2-S1-S1'	92.2 (1)
C4-P1-N2	110.0 (1)	S1-N1-P2	119.4 (2)
C1-P2-C2	106.7 (2)	S1-N2-P1	122.0 (2)
C1-P2-N1	113.3 (1)		

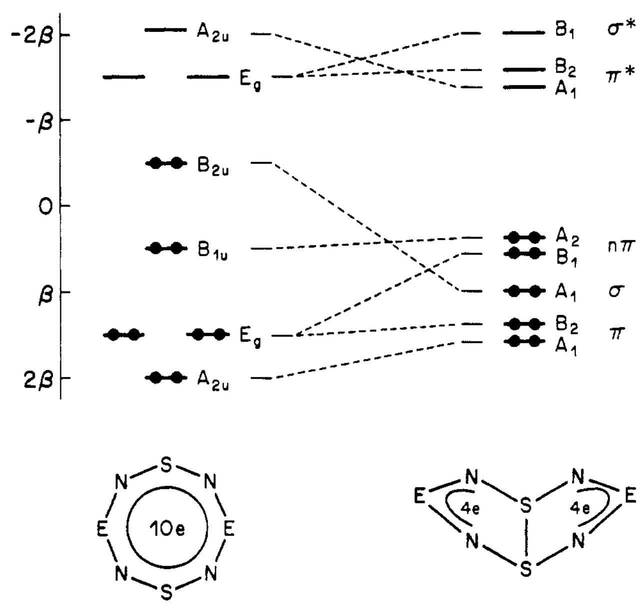

Figure 2. Orbital correlation diagram for the planar and puckered models of the eight-membered ring systems $E(NSN)_2E$, where $\alpha_E = \alpha_S$.

(7) In $(Me_2PN)_4$ the *gem*-methyl groups are crystallographically nonequivalent,[15] but they are statistically equivalent on the NMR time scale: Searle, H. J.; Dyson, J.; Paddock, N. L.; Ranganathan, T. N. *J. Chem. Soc., Dalton Trans.* **1975**, 203.
(8) Chivers, T.; Proctor, J. *Can. J. Chem.* **1979**, *57*, 1288.
(9) Ernest, I.; Holick, W.; Rihs, G.; Schomburg, G.; Shoham, G.; Wenkert, D.; Woodward, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1540.
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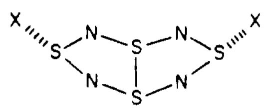
(11) (a) Sharma, B. D.; Donohue J. *Acta Crystallogr.* **1963**, *16*, 891. (b) De Lucia, M. L.; Coppens, P. *Inorg. Chem.* **1978**, *17*, 2336.
(12) Bragin, J.; Evans, M. V. *J. Chem. Phys.* **1969**, *51*, 268.
(13) Flues, W.; Scherer, O. J.; Weiss, J.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 379.

lographic mirror plane, the two sulfur and two nitrogen atoms form two four-membered planes that intersect at an angle of 114.9° (cf. 114° in $Me_2NC(NSN)_2CNMe_2$[9] and 120.4° in 1,5-$(Ph_3P{=}N)_2S_4N_4$[1]). The phosphorus atoms P1 and P2 lie out and an opposite sides of these planes by +0.194 and −0.479 Å, respectively. The difference in the positions of the phosphorus atoms appears to result from a balance of a short intramolecular contact between methyl carbons C1 and C3 of 3.99 Å and short intermolecular contacts of the type C1–C3 ($^1/_2 - x, y, -^1/_2 - z$), 3.64 Å, and C2–C4 ($1 - x, y, z$), 3.61 Å.

Because of the close S1–S1′ transannular interaction and the consequent angle strain associated with the PN_2S_2 rings, the geometry of the Me_2PN_2 units differs significantly from that found in methylphosphazene structures;[14] the mean endocyclic angles at phosphorus (108.6°) and nitrogen (120.7°) are smaller than in $(NPMe_2)_3$ ($\hat{P}_{endo}$ = 116.8°, $\hat{N}$ = 122.6°)[14] and $(NPMe_2)_4$ ($\hat{P}_{endo}$ = 119.8°, $\hat{N}$ = 132.0°).[15] The mean P–N distance (1.636 Å) is also significantly longer than in $(NPMe_2)_n$ (d(P–N) = 1.605 and 1.596 Å for n = 3 and 4, respectively).[14,15] While this elongation may in part be due to changes in σ hybridization, it is more probably the result of the relative weakness of the π bonds of the four-electron, three-center subunits in the $Me_2P(NSN)_2PMe_2$ structure (vide infra) as opposed to the π bonds found in the $(Me_2PN)_n$ series.

Electronic Structure and Bonding in $Me_2P(NSN)_2PMe_2$ and Related Eight-Membered Rings. The most interesting feature of the present structure is the existence of the short transannular S–S interaction. We have previously pointed out a qualitative correlation between the S–S distances in S–N bicyclic and cage molecules (e.g., **4** and **5**) and the ability of



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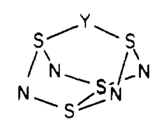
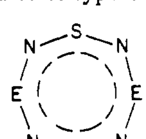
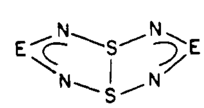


5

the 1,5 substituents (X = $Ph_3P{=}N$; Y = N^-, N^+, NSN) to remove π^*-electron density from the cage.[1] Bartetzko and Gleiter have illustrated the origin of the effect in terms of the influence of the π-donor or -acceptor properties of Y on the two potentially interacting sulfur diimide groups.[16] For molecules of type **6** the structural dichotomy is more acute.



6a



6b

Depending on the nature of E, the $E(NSN)_2E$ molecule can exist as either a planar ring structure **6a** (e.g., in $PhC(NSN)_2CPh$[9] and $S_4N_4^{2+}$[17]) or a butterfly-shaped structure with a cross-ring S–S bond, **6b** (e.g., in $Me_2P(NSN)_2PMe_2$ and $Me_2NC(NSN)_2CNMe_2$[9]).

We can understand the reasons for the existence of these two structural modifications by using the results of simple Hückel MO calculations. We begin by classifying the distribution of π electrons in the two limiting structures **6a** and **6b**. In the former the π system contains a total of ten electrons, this number being reduced to eight upon formation of a transannular S–S σ bond. The π electrons in **6b** are then separated into two formally isolated four-electron, three-center N⋯E⋯N units. The Hückel π energy levels associated with these two models will of course depend on the relative magnitudes of the three Coulomb parameters α_E, α_S, and α_N. The value of α_E will vary according to the electronegativity of the element and the orbital involved. This may be a phosphorus 3d (in $Me_2P(NSN)_2PMe_2$), a sulfur 3p (in $S_4N_4^{2+}$), or a carbon 2p (in $PhC(NSN)_2CPh$ and $Me_2NC(NSN)_2CNMe_2$), and for this series we can write $\alpha_S < \alpha_C < \alpha_P$. Figure 2 illustrates an orbital correlation diagram for the two models **6a** and **6b** for the simple case of $\alpha_E = \alpha_S$, i.e., as would be found in $S_4N_4^{2+}$. As described by Gleiter[18] and by Paddock and co-workers,[19] the π^* HOMO of the planar model transforms into the bonding S–S σ interaction of the folded ring. Changing the electronegativity of E has predictable effects on the two systems, the most sensitive orbital being the HOMO of the planar model, which is naturally stabilized by more electronegative values of α_E. The net consequences of this stabilization are illustrated in Figure 3, which shows a plot of Δ, the difference in the π-electron energy between the two models (Δ = π energy[**6a**] − π energy[**6b**]), as a function of α_E. It is important to stress that the magnitude of Δ has little absolute meaning by itself. It must be considered in combination with the potential contribution of the S–S σ bond in **6b** to the total binding energy, and the strength of the latter interaction remains undefined in the present calculations. Nonetheless, the trend in Δ with change in α_E serves to illustrate that with a greater electronegative perturbation at E the π system of **6a** is increasingly favored over that of **6b**. Thus, at some point the π energy of **6a** will be sufficient to outweigh the combined σ (S–S) and π energies of **6b**, leading to an overall preference for the planar structure. These qualitative conclusions correspond well with the observed geometries of $E(NSN)_2E$ structures. In $S_4N_4^{2+}$, where the electronegative perturbation is greatest, a planar conformation is expected and is found in a number of $S_4N_4^{2+}$ salts by X-ray structural determinations.[17] In molecules of the type $RC(NSN)_2CR$, the balance between the planar and folded conformations is sensitive to the nature of R. Thus when R = Ph the electronegativity of carbon is sufficient to favor the planar modification. However, when a π-donating ligand, e.g., R = NMe_2, is present, the π levels of the planar structure (principally the HOMO) will be raised in energy, shifting the balance in favor of the folded form. In phosphorus-containing heterocycles of the type $R_2P(NSN)_2PR_2$, α_P is expected to be algebraically large, and folded structures would be expected, as found in the present case. However, it is conceivable that through modification of the ligands on phosphorus, e.g., by replacement of the methyl groups by fluorine, the electronegative perturbation might be sufficient to induce planarity (cf. $(NPMe_2)_4$[15] vs. $(NPF_2)_4$[20]). We are currently exploring possible preparative routes to $F_2P(NSN)_2PF_2$ in order to test this hypothesis.

Proposed Mechanism for the Formation of $Me_2P(NSN)_2PMe_2$. We have previously demonstrated that the thermolysis of S–N rings occurs via loss of either N_2S (e.g., $S_3N_3^-$,[21] $Ph_3P{=}N{-}S_3N_3$[22]) or S_2N_2 units (e.g., $Ph_3As{=}$

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(22) Chivers, T.; Oakley, R. T.; Cordes, A. W.; Swepston, P. N. *J. Chem. Soc., Chem. Commun.* **1980**, 35.

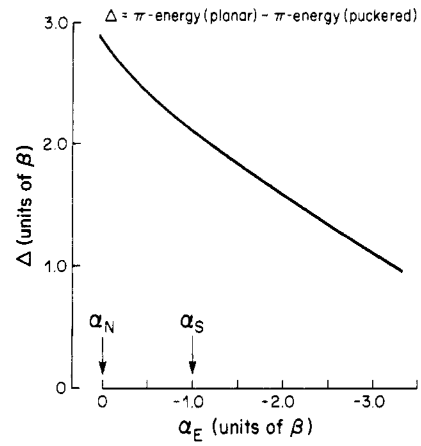

Figure 3. Difference Δ (=π energy[**6a**] − π energy[**6b**]) as a function of α_E, Coulomb parameter of E. Calculations were done with the assumption that $\alpha_N = \alpha_S + \beta$. Values of α_E are assigned relative to α_N as an arbitrary zero point. All β's were assumed equal.

N—S_3N_3).[23] The thermal decomposition of $Me_2PS_2N_3$ results in the products indicated in the equation

$$Me_2PS_2N_3 \rightarrow S_4N_4 + (Me_2PN)_3 + (Me_2PN)_4 + Me_2P(NSN)_2PMe_2$$

As determined by ^{31}P NMR spectroscopy the major phosphorus-containing product is $Me_2P(NSN)_2PMe_2$. In addition, $(Me_2PN)_3$ and a very small amount of $(Me_2PN)_4$ are formed. The formation of S_4N_4 suggests the elimination of S_2N_2 during the thermolysis since it is known that S_2N_2 dimerizes in the presence of nucleophiles.[24] The unimolecular elimination of S_2N_2 would imply the transient formation of Me_2PN monomer,[25] which could account for the formation of $(Me_2PN)_3$ and $(Me_2PN)_4$. Furthermore, the eight-membered ring $Me_2P(NSN)_2PMe_2$ might result from the insertion of Me_2PN monomer into an S–N bond of the six-membered ring, $Me_2PS_2N_3$. However, the occurrence of a bimolecular process as the first step in the thermal decomposition of $Me_2PS_2N_3$ cannot be excluded.

Conclusion

In 10-π-electron, eight-center systems the π electrons may be accommodated in a planar structure, e.g., $S_4N_4^{2+}$ and PhC(NSN)$_2$CPh, or by forming a butterfly conformation with a 1,5-transannular S–S σ bond, e.g., $Me_2NC(NSN)_2CNMe_2$. The latter structure is adopted in the case of Me_2P-$(NSN)_2PMe_2$, but the extent of the transannular interaction is likely to be sensitive to the nature of the substituents on phosphorus. It is possible that planar structures will be found for molecules containing strongly electron-withdrawing substituents on phosphorus.

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Registry No. $Me_2P(NSN)_2PMe_2$, 80106-10-1; $Me_2PS_2N_3$, 80126-92-7.

Supplementary Material Available: Listings of parameters for the hydrogen atoms (Table SI), thermal parameters (Table SII), and calculated and observed structure factors for $Me_2P(NSN)_2PMe_2$ (12 pages). Ordering information is given on any current masthead page.

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(25) The finite existence of Me_2PN monomer is a debatable point. The thermal degradation of *N*-silylphosphoranimines, $Me_3SiN{=}PMe_2X$, is known to give polymeric $(Me_2PN)_n$ ($X = OCH_2CF_3$, $n \sim 650$) or $(Me_2PN)_4$ (X = Br). The mechanisms of the chain-lengthening or cyclization reactions are unknown. Although a monomeric precursor is possible, bimolecular processes seem equally plausible. Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848.