Angewandte
International Edition Chemie

DOI: 10.1002/anie.201409868

Main-Group-Element Heterocycles

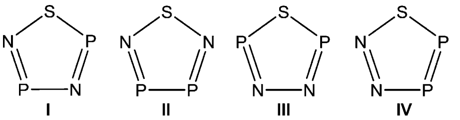
SN_2P_2: A Neutral Five-Membered Sulfur–Pnictogen(III) Ring**

Xiaoqing Zeng, Hongmin Li, Hailong Sun, Helmut Beckers,* Helge Willner, and Henry F. Schaefer III**

Abstract: *The novel aromatic ring compound 2,4-diphospha-3,5-diaza-thiole (cyclo-SNPNP) was synthesized via flash pyrolysis of $SP(N_3)_3$ and characterized by IR spectroscopy and ^{15}N isotope labeling. Quantum chemical computations indicate its formation by head-to-tail dimerization of SNP and subsequent elimination of a sulfur atom from the highly unstable boatlike six-membered-ring compound cyclo-SNPSNP.*

Inorganic main-group heterocycles have attracted strong interest in computational and synthetic chemistry, as well as in materials science.[1] In the past few decades, more and more heterocycles containing Group 15 (N, P) and Group 16 (O, S) elements bearing novel structural and bonding properties have been prepared.[1,2] In contrast, ligand-free neutral heterocycles of these elements with 6π electrons are barely known experimentally, due to either low dissociation barriers or lack of synthetic approaches. Examples are the five-membered rings ON_4,[3] SN_4,[4] OP_4,[5] and SP_4,[6] and the six-membered rings N_6,[7] P_6,[8] and P_3N_3.[9] Their structures and reactivities have been extensively explored using quantum chemical computations. However, the cationic binary sulfur–nitrogen 6π electron ring $S_3N_2^{2+}$ (1,2,4,3,5-trithiadiazole dication) has been structurally characterized.[10]

Among these neutral planar 6π electron ring molecules, only the C_{2v}-symmetric five-membered OP_4 ring (oxatetraphosphole) was tentatively identified by IR spectroscopy (^{16}O: $\tilde{\nu} = 825.7\ cm^{-1}$, ^{18}O: $\tilde{\nu} = 790.2\ cm^{-1}$) from the products-generated by the photolysis of phosphorus/ozone mixtures in solid Ar or by laser ablation of P_4O_{10}.[11] Computationally, the C_{2v}-symmetric ring isomer was predicted to be the global minimum on the potential energy surface (PES) of OP_4.[5a] This is true also for the heavier C_{2v}-symmetric five-membered congener, SP_4, which, however, remains experimentally unknown.[6] In contrast, the structurally related and isoelectronic analogue SN_2P_2, having four isomeric ring structures (Scheme 1), has been overlooked by both theory and experiment.



Scheme 1. Four five-membered-ring isomers of SN_2P_2.

Inspired by our contributions in inorganic main-group ring systems like diazirinone (*cyclo*-N_2CO),[12] thiazaphosphirine (*cyclo*-SNP),[13] and isomers of disulfur dinitride,[14] we report on the formation of the novel 6π electron ring SN_2P_2 (**I**) through dimerization of SNP followed by sulfur elimination.

Recently, 1,3-dipolar SNP was found to be readily produced either by photolysis of matrix-isolated $SP(N_3)_3$ or by flash pyrolysis of the same precursor in the gas phase.[13] Through the latter approach it is possible to study its dimerization. Dimerization of its congeners N_2O, N_2S, and OPN has not yet been observed, although their formal dimers, N_4O_2,[15] N_4S_2,[4a] and $O_2P_2N_2$,[16] have been studied theoretically.

Gaseous SNP was produced by flash pyrolysis of $SP(N_3)_3$ diluted in Ar (about 1:1000) at ca. 1000 °C. The products, including the possible SNP dimer, were deposited as a matrix at 16 K (for experimental details, see the Supporting Information). Analysis of the IR spectra (Figure S1, Supporting Information) shows the presence of SNP, PN, SN_2, SN, PS, and HN_3. In addition, one set of IR bands (marked **I** in Figure 1) at $\tilde{\nu} = 1045.4$, 910.7, and 713.9 cm^{-1} was found in the mid-IR region, and their intensities increased with prolonged deposition time. These bands were reproduced in Ne matrix, but

---

[*] Prof. Dr. X. Q. Zeng, H. M. Li, H. L. Sun
The Key Lab of Health Chemistry and Molecular Diagnosis of Suzhou, College of Chemistry
Chemical Engineering and Materials Science, Soochow University
Suzhou 215123 (China)
E-mail: xqzeng@suda.edu.cn

Dr. H. Beckers
Freie Universität Berlin
Institut für Chemie und Biochemie
14195 Berlin (Germany)
E-mail: h.beckers@fu-berlin.de

Prof. Dr. H. Willner
FB C—Anorganische Chemie
Bergische Universität Wuppertal
42119 Wuppertal (Germany)

Prof. Dr. H. F. Schaefer III
Center for Computational Quantum Chemistry
University of Georgia, Athens, GA 30677 (USA)
E-mail: ccq@uga.edu

[**] This research was supported by the National Natural Science Foundation of China (21372173, 21422304), the Project of Scientific and Technologic Infrastructure of Suzhou (SZS201207), the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), and the Deutsche Forschungsgemeinschaft (WI 663/26-1). X.Q.Z. thanks H.W. for a research stay in his lab. H.F.S. was supported by the U.S. National Science Foundation (grant CHE-1361178) and thanks the Alexander von Humboldt Foundation for the opportunity to visit the Ludwig-Maximilians University (Munich).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201409868.

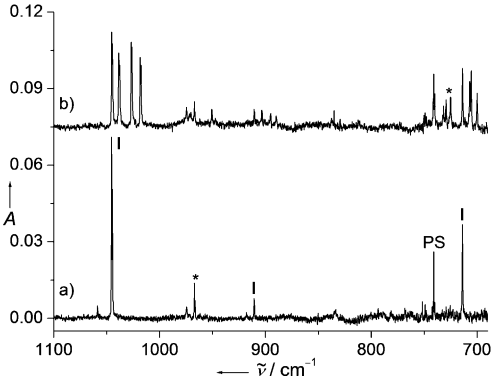


Figure 1. Mid-IR spectra ($\tilde{\nu}=1100$–$690\ \text{cm}^{-1}$, in absorbance) of Ar-matrix-isolated pyrolysis products of $SP(N_3)_3$ (a) and of ^{15}N-labeled $SP(N_3)_3$ (b). IR bands of **I**, diatomic PS, and an unknown species (*) are indicated.

their positions shifted to $\tilde{\nu}=1043.2$, 908.5, and $715.9\ \text{cm}^{-1}$, respectively. In contrast to the facile photoisomerization of SNP to SPN, the carrier of these new bands is only weakly depleted by UV irradiation ($\lambda=255$ nm or >280 nm). It should be noted that none of these bands was observed in photolysis experiments of matrix-isolated $SP(N_3)_3$.[13] A ^{15}N-labeled $SP(N_3)_3$ sample, prepared by using 1-^{15}N sodium azide (98 atom% ^{15}N), was also used for a pyrolysis experiment. The mid-IR spectrum of the matrix-isolated decomposition products are shown in Figure 1 b. The IR bands of the known nitrogen-containing species SNP, PN, SN_2, SN, and HN_3 display distinct doublet splittings. In contrast, the three new IR bands clearly show quartet splittings upon ^{15}N-labeling (Figure 1 b).

The far-IR spectrum of the pyrolysis products of $SP(N_3)_3$ was recorded using a liquid-helium-cooled Bolometer detector. In addition to the IR bands of SNP at $\tilde{\nu}=358.1$ and $354.4\ \text{cm}^{-1}$ (different matrix sites)[13] three new bands at $\tilde{\nu}=520.9$, 459.1, and $389.8\ \text{cm}^{-1}$ were observed (Figure 2 a). In ^{15}N-labeling experiments, the bands at $\tilde{\nu}=520.9$ and $389.8\ \text{cm}^{-1}$ display quartet ^{15}N-isotope splitting patterns (Figure 2 b) similar to those in the mid-IR spectrum (Figure 1 b). However, the band at $\tilde{\nu}=459.1\ \text{cm}^{-1}$ splits into a doublet at $\tilde{\nu}=458.8$ and $456.9\ \text{cm}^{-1}$ (Figure 2 b). Both components revealed a full-width at half-maximum (FWHM) of $\Delta\tilde{\nu}=1.1\ \text{cm}^{-1}$, and they are broadened compared to the band of the natural sample, indicating an unresolved ^{15}N quartet pattern. The quartet ^{15}N isotopic pattern of these new bands corresponds to a carrier containing two structurally non-equivalent nitrogen atoms. Since the main pyrolysis product of $SP(N_3)_3$ is SNP, its dimer would be expected to be the predominant secondary product when a highly diluted precursor is applied in a noble gas (Ar or Ne, estimated ratio of 1:1000). Indeed, the IR band intensities of the unknown carrier relative to those of SNP are clearly lower at higher pyrolysis temperatures (Figure S2, Supporting Information).

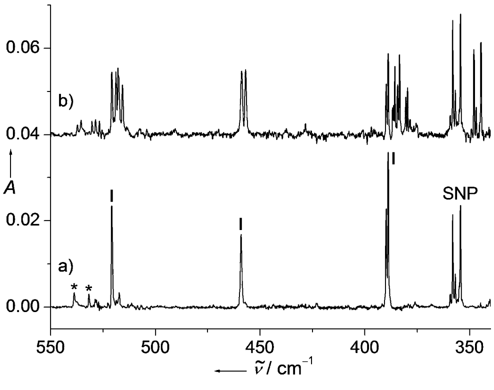


Figure 2. Far-IR spectra ($\tilde{\nu}=550$–$340\ \text{cm}^{-1}$, in absorbance) of Ar-matrix-isolated pyrolysis products of $SP(N_3)_3$ (a) and of ^{15}N-labeled $SP(N_3)_3$ (b). IR bands of I, triatomic SNP, and an unknown species (*) are indicated.

To aid the assignment, theoretical computations on SNP dimers were performed (Figure S3, Supporting Information). Among these structures, only the boatlike six-membered ring *cyclo*-SNPSNP (Figure 3) with C_2 symmetry can be considered to be a true dimer of SNP formed by head-to-tail dimerization (Tables S1 and S2, Supporting Information). All other isomers are deemed to be products formed from the reactions SNP + SPN or SPN + SPN. However, it should be pointed out that triatomic SPN was not found among the pyrolysis products of $SP(N_3)_3$. Isomerization from SNP to the higher-energy isomer SPN via *cyclo*-SNP is unlikely under the pyrolysis conditions due to an activation barrier of more than $\Delta G=200\ \text{kJ mol}^{-1}$ (B3LYP/6-311 + G(3df)).[13] A boatlike six-membered ring compound *cyclo*-ONPONP was also proposed based on theory as the most likely product formed by the dimerization of closely related OPN.[16] However, the occurrence of two structurally equivalent nitrogen atoms in *cyclo*-SNPSNP rules out this species as the carrier for the new IR bands. In addition, theoretically predicted IR spectra for the $S_2P_2N_2$ isomers (Tables S3–S7, Supporting Information) do not agree with the observation.

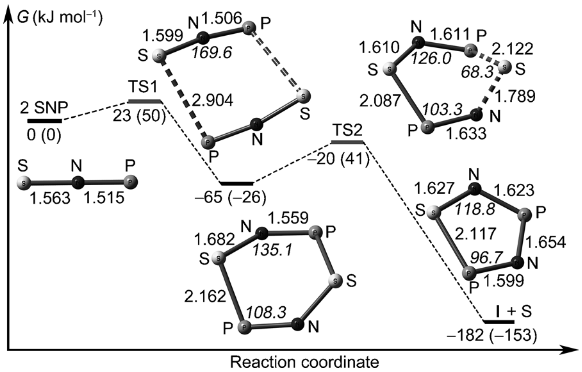


Figure 3. Formation pathway of **I** from SNP obtained at the CBS-QB3 level of theory. Relative energies, ΔG(298 K), are given in kJ mol^{-1} (B3LYP/6-311 + G(3df) values in parentheses). Computed bond lengths [Å] and angles [°] at the B3LYP/6-311 + G(3df) level are indicated.

Given the nonequivalence of the nitrogen atoms in the carrier and also the involvement of *cyclo*-SNPSNP, the most likely carrier is the five-membered ring *cyclo*-SNPNP (**I**, Scheme 1). It can be regarded as the decomposition product

Table 1: Observed and calculated IR band positions and ^{15}N isotopic shifts (cm^{-1}) of *cyclo*-SNPNP (C_s) relative to the natural compound.

	ν_i		$\Delta\nu_i(SNP^{15}NP)$		$\Delta\nu_i(S^{15}NPNP)$		$\Delta\nu_i(S^{15}NP^{15}NP)$		Assignment,[f]
B3LYP[a]	MP2[b]	obsd.[c]	calcd	obsd[e]	calcd[d]	obsd[e]	calcd[d]	obsd[e]	description of modes
1066 (76)	1054 (52)	1045.4 (100)	19.3	18.6	7.0	6.8	28.1	27.0	a′, ν_1, ν(NP), in phase
927 (13)	918 (32)	910.7 (9)	8.0	7.2	17.7	15.7	24.0	20.9	a′, ν_2, ν(NP), o.o.phase
754 (4)	751 (2)		4.3		8.9		17.2		a′, ν_3, breathing
729 (62)	707 (33)	713.9 (37)	10.0	8.4	7.4	6.1	13.4	13.9	a′, ν_4, ν_{as}(NPN)
532 (12)	520 (11)	520.9 (20)	2.1	1.9	3.3	3.2	5.5	5.2	a′, ν_5, δ(NPN)
463 (9)	456 (10)	459.1 (17)	2.9	2.2	1.1	<0.5	3.9	2.2	a′, ν_6, δ(NPS)
430 (3)	451 (<1)		0.1		0.2		0.3		a′, ν_7, ν(SP)
401 (19)	401 (18)	389.8 (32)	3.6	3.2	5.4	5.4	9.6	9.3	a″, ν_8, γ(NPN)
349 (<1)	356 (<1)		4.7		3.1		7.1		a″, ν_9, o.o.p.(NSPN)

[a] Calculated IR frequencies (cm^{-1}) and IR intensities (in parentheses, $km\,mol^{-1}$) at the B3LYP/6-311+G(3df) level. [b] Calculated IR frequencies (cm^{-1}) and IR intensities (in parentheses, $km\,mol^{-1}$) at the MP2/6-311+G(3df) level. [c] Observed IR band positions in Ar matrix at 16 K with relative intensities (in parentheses) based on integrated areas of all matrix sites. [d] Calculated $^{14/15}N$ isotopic shifts at the B3LYP/6-311+G(3df) level. [e] Observed $^{14/15}N$ isotopic shifts in Ar matrix. [f] Tentative assignment for the vibrational modes according to calculated displacement vectors (o.o.p.: out of plane, o.o.phase = out of phase; see Table S12, Supporting Information).

of a SNP dimer through sulfur-atom elimination. This assumption is supported by the good agreement between the observed and computed IR spectra and ^{15}N-isotopic shifts for **I**, which are collected in Table 1. For comparison, the spectra and relative energies of all isomers of SP_2N_2 were calculated (Figure S4 and Tables S8–13, Supporting Information). Compared to **I,** the other isomers are higher in energy and their computed IR spectra are quite different to the observed spectra.

As can be seen in Table 1, the positions of the six strongest bands of **I** are reasonably well predicted by DFT/B3LYP and ab initio MP2 calculations. According to the ^{15}N-isotopic shifts and calculated vibrational displacement vectors (B3LYP/6-311+G(3df)), the most intense feature, $\tilde{\nu}=1045.4\,cm^{-1}$ ($\Delta\nu(^{14/15}N)=18.6$, 6.8, and $27.0\,cm^{-1}$), is mainly attributed to the N–P stretching vibrations. Its frequency is lower than those found in *trans*-FP=NF ($\tilde{\nu}=1116.8\,cm^{-1}$, $\Delta\nu(^{14/15}N)=25.3\,cm^{-1}$, matrix IR)[17] and P_3N_3 ($\tilde{\nu}=1137\,cm^{-1}$, $\Delta\nu(^{14/15}N)=10$, 20, and $30\,cm^{-1}$, matrix IR).[9b] The out-of-phase N–P vibration occurs at $\tilde{\nu}=910.7\,cm^{-1}$, which is close to the average of those observed for the five-membered ring of 4-bis(trimethylsilyl)amino-1,2,4,3,5-triazadiphosphole RN_3P_2 ($\tilde{\nu}=(PN)=996$ and $843\,cm^{-1}$, solid Raman).[2e] The description of the modes in Table 1 is somewhat tentative, because discrimination between bond-stretching and ring-deformation modes is difficult. In-plane and out-of-plane NPN deformations appear at $\tilde{\nu}=520.9$ and $389.8\,cm^{-1}$, respectively. The former band exhibits a very weak feature at $\tilde{\nu}=518.7\,cm^{-1}$, corresponding to the naturally abundant ^{34}S isotopologue (4.2%), and the shift ($2.2\,cm^{-1}$) agrees with the prediction of $\Delta\tilde{\nu}=2.0\,cm^{-1}$. The NPS deformation ($\delta$-(NPS)) occurs at $\tilde{\nu}=459.1\,cm^{-1}$, and the associated $^{32/34}S$ isotopic shift is $\Delta\tilde{\nu}=2.3\,cm^{-1}$ (calculated: $3.0\,cm^{-1}$). The ring-breathing mode and the S–P stretching vibration, predicted at $\tilde{\nu}=754$ and $430\,cm^{-1}$ (B3LYP/6-311+G(3df)), respectively, were not observed in the spectrum probably due to their very low IR intensity. The IR band positions of **I** ($\tilde{\nu}=1045.4$, 910.7, 713.9, 520.9, 459.1, and $389.8\,cm^{-1}$) are comparable to those of the isoelectronic 6π ring $S_3N_2^{2+}$ (IR: $\tilde{\nu}=1051$, 968, 668, 483, and $438\,cm^{-1}$; Raman: $\tilde{\nu}=1060$, 972, 780, 490, and $395\,cm^{-1}$) as observed in solid $[S_3N_2][AsF_6]_2$.[10]

To account for the gas-phase formation of **I** from SNP, computations on the reaction pathway using the CBS-QB3 and B3LYP/6-311+G(3df) methods were carried out (Figure 3). The transition states for the dimerization of SNP (TS1) and the subsequent sulfur elimination (TS2) were located, and confirmed by an intrinsic reaction coordinate (IRC) analysis (Figure S5 and Table S14, Supporting Information).

Similar to cycloaddition reactions of most 1,3-dipoles,[18] a concerted approach for the dimerization of SNP was found. The transition state (TS1) can be regarded as a weakly bound head-to-tail SNP complex with C_2 symmetry. Compared to the linear reactant, the two SNP units in TS1 are slightly bent ($\angle SNP=169.6°$) and face each other, with rather long S–P bond lengths of 2.904 Å. The weak interaction also alters the S–N and N–P bond lengths; the former elongated from 1.569 Å in SNP to 1.599 Å in TS1, while the latter shortened from 1.515 Å to 1.506 Å. These changes are consistent with the suggestion of an increased diradical character and an enhanced reactivity by distortion of an 1,3-dipole from its equilibrium linear structure.[19]

The low-lying bending vibration of SNP ($\tilde{\nu}=358.1\,cm^{-1}$)[13] and the small bond distortion of the SNP moieties in TS1 are consistent with a rather low CBS-QB3 activation barrier of $\Delta G=23\,kJ\,mol^{-1}$ for the dimerization. As suggested by recent theoretical studies, mainly the distortion energy and the interaction energy of the distorted fragments in the TS structure contributes to the activation barrier of cycloaddition reactions involving 1,3-dipoles.[20] The low activation energy for the cycloaddition of SNP is in contrast to the predicted much higher barrier of about $\Delta E=110\,kJ\,mol^{-1}$ for the 1,3-dipolar cycloaddition of its lighter congener N_2O to alkynes,[18b] which was observed only very recently.[18a]

In the subsequent decomposition of *cyclo*-SNPSNP, one sulfur atom is expelled from the near-planar NPSNP framework in the transition state (TS2), which corresponds to a CBS-QB3 activation barrier of $\Delta G=45\,kJ\,mol^{-1}$. Such a low barrier indicates a facile thermal fragmentation of six-membered *cyclo*-SNPSNP at the pyrolysis conditions into *cyclo*-SNPNP (**I**) and atomic sulfur with an energy release of

$\Delta G = 117$ kJ mol^{-1}. The sulfur atoms dimerise to disulfur (S_2) during matrix deposition as detected by UV spectroscopy.[13] In contrast, **I** is thermally persistent in the gas phase since its potential fragmentation products SPN + PN, SNP + PN, and P_2N_2[21] + $^1/_2$ S_2 are considerably higher in energy (CBS-QB3: $\Delta G = 272$, 201, and 248 kJ mol^{-1}, respectively).

In conclusion, a novel neutral inorganic sulfur–pnictogen(III) five-membered ring, *cyclo*-SNPNP, bearing 6 π electrons, was produced in the gas phase. Its identification was established by IR spectroscopy, ^{15}N labeling, and computations. Its formation is computationally rationalized by a facile concerted head-to-tail dimerization of 1,3-dipolar SNP to a six-membered-ring intermediate *cyclo*-SNPSNP, followed by sulfur elimination.

Received: October 8, 2014
Published online: December 4, 2014

Keywords: flash pyrolysis · heterocycles · IR spectroscopy · matrix isolation · sulfur–pnictogen compounds

---

[1] See, very recent examples: a) G. He, O. Shynkaruk, M. W. Lui, E. Rivard, *Chem. Rev.* **2014**, *114*, 7815 – 7880; b) T. Chivers, R. Laitininen in *Handbook of Chalcogen Chemistry*: *New Perspectives in Sulfur*, *Selenium and Tellurium*, *Vol. 1*, *2nd ed.* (Eds.: F. A. Devillanova, W. W. du Mont), RSC, Cambridge, **2013**, pp. 191 – 237.

[2] See, for examples: a) C. Hering, A. Schulz, A. Villinger, *Chem. Sci.* **2014**, *5*, 1064 – 1073; b) S. S. Sen, J. Hey, M. Eckhardt, R. Herbst-Irmer, E. Maedl, R. A. Mata, H. W. Roesky, M. Scheer, D. Stalke, *Angew. Chem. Int. Ed.* **2011**, *50*, 12510 – 12513; *Angew. Chem.* **2011**, *123*, 12718 – 12721; c) T. Köchner, S. Riedel, A. J. Lehner, H. Scherer, I. Raabe, T. A. Engesser, F. W. Scholz, U. Gellrich, P. Eiden, R. A. Paz Schmidt, D. A. Plattner, I. Krossing, *Angew. Chem. Int. Ed.* **2010**, *49*, 8139 – 8143; *Angew. Chem.* **2011**, *123*, 8316 – 8320; d) M. S. Balakrishna, D. J. Eisler, T. Chivers, *Chem. Soc. Rev.* **2007**, *36*, 650 – 664; e) S. Herler, P. Mayer, J. Schmedt auf der Grünne, A. Schulz, A. Villinger, J. J. Weigand, *Angew. Chem. Int. Ed.* **2005**, *44*, 7790 – 7793; *Angew. Chem.* **2005**, *117*, 7968 – 7971; f) T. Chivers, *Acc. Chem. Res.* **1984**, *17*, 166 – 171.

[3] J. M. Galbraith, H. F. Schaefer, *J. Am. Chem. Soc.* **1996**, *118*, 4860 – 4870, and references therein.

[4] a) G. H. Zhang, Y. F. Zhao, J. I. Wu, P. v. R. Schleyer, *Inorg. Chem.* **2012**, *51*, 13321 – 13327; b) D. Glossman-Mitnik, *Theor. Chem. Acc.* **2007**, *117*, 57 – 68; c) T. M. Klapötke, A. Schulz, *Polyhedron* **1996**, *15*, 4387 – 4390.

[5] a) B. Engels, A. R. S. Valentim, S. D. Peyerimhoff, *Angew. Chem. Int. Ed.* **2001**, *40*, 378 – 381; *Angew. Chem.* **2001**, *113*, 393 – 396; b) L. L. Lohr, *J. Phys. Chem.* **1990**, *94*, 4832 – 4835; c) S. A. Jarrett-Sprague, I. H. Hillier, I. R. Gould, *Chem. Phys.* **1990**, *140*, 27 – 33.

[6] P. J. Bruna, S. D. Peyerimhoff, *Chem. Phys.* **1991**, *149*, 325 – 331.

[7] See, for examples: a) H. Huber, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 64 – 65; *Angew. Chem.* **1982**, *94*, 71 – 72; b) P. Saxe, H. F. Schaefer, *J. Am. Chem. Soc.* **1983**, *105*, 1760 – 1764; c) M. Tobita, R. J. Bartlett, *J. Phys. Chem. A* **2001**, *105*, 4107 – 4113.

[8] a) T. R. Galeev, A. I. Boldyrev, *Phys. Chem. Chem. Phys.* **2011**, *13*, 20549 – 20556; b) D. S. Warren, B. M. Gimarc, *J. Am. Chem. Soc.* **1992**, *114*, 5378 – 5385.

[9] a) R. Ahlrichs, M. Bär, H. S. Plitt, H. Schnöckel, *Chem. Phys. Lett.* **1989**, *161*, 179 – 184; b) R. Atkins, P. L. Timms, *Spectrochim. Acta* **1977**, *33*, 853 – 857.

[10] See, for examples: a) T. Chivers in *A Guide to Chalcogen-Nitrogen Chemistry*, World Scientific, London, **2005**, pp. 191 – 237; b) W. V. F. Brooks, T. S. Cameron, S. Parsons, J. Passmore, M. J. Schriver, *Inorg. Chem.* **1994**, *33*, 6230 – 6241; c) G.-H. Zhang, Y. F. Zhao, J. I. Wu, P. v. R. Schleyer, *Inorg. Chem.* **2009**, *48*, 6773 – 6780; d) B. M. Gimarc, D. S. Warren, *Inorg. Chem.* **1991**, *30*, 3276 – 3280.

[11] a) L. Andrews, R. Withnall, *J. Am. Chem. Soc.* **1988**, *110*, 5605 – 5611; b) Z. Mielke, L. Andrews, *Inorg. Chem.* **1990**, *29*, 2773 – 2779; c) M. McCluskey, L. Andrews, *J. Phys. Chem.* **1991**, *95*, 2988 – 2994; d) M. McCluskey, L. Andrews, *J. Phys. Chem.* **1991**, *95*, 3545 – 3549; e) C. W. Bauschlicher, Jr., M. Zhou, L. Andrews, *J. Phys. Chem. A* **2000**, *104*, 3566 – 3571.

[12] a) X. Q. Zeng, H. Beckers, H. Willner, J. F. Stanton, *Angew. Chem. Int. Ed.* **2011**, *50*, 1720 – 1723; *Angew. Chem.* **2011**, *123*, 1758 – 1761; b) X. Q. Zeng, H. Beckers, H. Willner, J. F. Stanton, *Eur. J. Inorg. Chem.* **2012**, 3403 – 3409.

[13] X. Q. Zeng, H. Beckers, H. Willner, J. S. Francisco, *Angew. Chem. Int. Ed.* **2012**, *51*, 3334 – 3339; *Angew. Chem.* **2012**, *124*, 3390 – 3395.

[14] a) A. Perrin, A. F. Antognini, X. Q. Zeng, H. Beckers, H. Willner, G. Rauhut, *Chem. Eur. J.* **2014**, *20*, 10323 – 10331; b) X. Q. Zeng, A. F. Antognini, H. Beckers, H. Willner, *Angew. Chem. Int. Ed.* **2014**, DOI: 10.1002/anie.201407538; *Angew. Chem.* **2014**, DOI: 10.1002/ange.201407538.

[15] a) R. D. Harcourt, *J. Mol. Struct. THEOCHEM* **1995**, *342*, 51 – 57; b) M. P. Doyle, J. J. Maciejko, S. C. Busman, *J. Am. Chem. Soc.* **1973**, *95*, 952 – 953.

[16] R. D. Davy, Y. Xie, H. F. Schaefer, *J. Am. Chem. Soc.* **1991**, *113*, 4136 – 4138.

[17] X. Q. Zeng, H. Beckers, H. Willner, *Angew. Chem. Int. Ed.* **2009**, *48*, 4828 – 4831; *Angew. Chem.* **2009**, *121*, 4922 – 4925.

[18] a) K. Banert, O. Plefka, *Angew. Chem. Int. Ed.* **2011**, *50*, 6171 – 6174; *Angew. Chem.* **2011**, *123*, 6295 – 6298; b) L. T. Nguyen, F. D. Proft, A. K. Chandra, T. Uchimaru, M. T. Nguyen, P. Geerlings, *J. Org. Chem.* **2001**, *66*, 6096 – 6103.

[19] B. Braida, C. Walter, B. Engels, P. C. Hiberty, *J. Am. Chem. Soc.* **2010**, *132*, 7631 – 7637.

[20] a) D. H. Ess, K. N. Houk, *J. Am. Chem. Soc.* **2008**, *130*, 10187 – 10198; b) B. Engels, M. Christl, *Angew. Chem. Int. Ed.* **2009**, *48*, 7968 – 7970; *Angew. Chem.* **2009**, *121*, 8110 – 8112; c) I. Fernánsez, F. P. Cossío, F. M. Bickelhaupt, *J. Org. Chem.* **2011**, *76*, 2310 – 2314.

[21] O. Kwon, P. M. Almond, M. L. McKee, *J. Phys. Chem. A* **2002**, *106*, 6864 – 6870.