IR Spectroscopy

Deutsche Ausgabe: DOI: 10.1002/ange.201510105
Internationale Ausgabe: DOI: 10.1002/anie.201510105

Gas-Phase Generation and Decomposition of a Sulfinylnitrene into the Iminyl Radical OSN

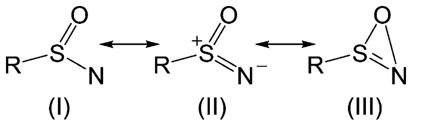
*Zhuang Wu, Dingqing Li, Hongmin Li, Bifeng Zhu, Hailong Sun, Joseph S. Francisco, and Xiaoqing Zeng**

Abstract: *The dipolar oxathiazyne-like sulfinylnitrene RS(O)N, a highly reactive α-oxo nitrene, has been rarely investigated. Upon flash vacuum pyrolysis of sulfinyl azide $CF_3S(O)N_3$ at 350°C, an elusive sulfinylnitrene $CF_3S(O)N$ was generated in the gas phase in its singlet ground state and was characterized by matrix-isolation IR spectroscopy. Further fragmentation of $CF_3S(O)N$ at 600°C produced CF_3 and a novel iminyl radical OSN, an SO_2 analogue, which were unambiguously identified by IR spectroscopy. Consistent with the experimental observations, DFT calculations clearly support a stepwise decomposition mechanism of $CF_3S(O)N_3$.*

Nitrenes are highly reactive intermediates featuring a neutral monovalent nitrogen atom. As a result of their importance in chemistry and biology, the synthesis, reactivity, and applications of nitrenes have been frequently reviewed in the past few decades.[1] Generally, nitrene can be straightforwardly generated from the decomposition of the corresponding azide by N_2 elimination upon photolysis or pyrolysis. However, because of facile intramolecular or intermolecular reactions, nitrenes are largely transient species and their direct detection usually requires ultrafast spectroscopy or cryogenic matrix-isolation techniques despite the fact that their existence, in some cases, bas been established by in situ chemical trapping reactions in solution.[1,2]

Singlet nitrenes can be rendered more stable by electron donation to the electron-deficient nitrene center. The donation may come from the lone pair of the geminal atom such as oxygen (in α-oxo nitrenes RC(O)N,[3] $R_2P(O)N$,[4] and RS$(O)_2N$[5]) and sulfur (in the heavier analogues RC(S)N[6] and $R_2P(S)N$[7]). Another type of effective stabilizing interaction is the delocalization of the lone pair from the atom which is directly bonded to the nitrene center, such as in aminonitrene (R_2N-N),[8] sulfenylnitrene (RS-N),[9] and phosphinonitrene (R_2P-N).[10] These compounds are singlet nitrenes with favorable Lewis resonance structures of diazene, thiazyne, and phosphazene, respectively.[11]

Sulfinylnitrene RS(O)N was suggested in the 1980s by Maricich et al. to be the key intermediate in the decomposition of benzenesulfinyl azide.[12] They found it to be completely different from the carbonyl nitrene, that is, it is reluctant to undergo rearrangement and insertion reaction towards C−H bonds but combines with sulfoxide to form sulfimides. This reactivity is rationalized by a dipolar oxathiazyne structure of the nitrene formed by the delocalization of the sulfur lone pair to the nitrene center (Scheme 1).



Scheme 1. Possible resonance structures of sulfinylnitrene.

However, because of the unusually low stability of sulfinyl azides, sulfinylnitrene remains experimentally unexplored.

In 2011, we showed that the decomposition of α-oxo azides not only produces the corresponding nitrenes, but their further fragmentation offers unique access to some fundamentally important small molecules like *cyclo*-N_2CO[13] and OPN.[14] Particularly, the generation of O_2SN,[15] an analogue of SO_3, from the flash vacuum pyrolysis (FVP) of $CF_3S(O)_2N_3$ by fragmentation of the weak $F_3C^{\delta+}$–$S^{\delta+}$ bond in $CF_3S(O)_2N$ inspired us to investigate the decomposition of the closely related $CF_3S(O)N_3$. Since the $F_3C^{\delta+}$–$S^{\delta+}$ bond in $CF_3S(O)N$ is also expected to be weak because of a dominant contribution of the oxathiazyne resonance structure (Scheme 1), its fragmentation would provide access to triatomic OSN,[16] a fundamentally important species in sulfur–nitrogen chemistry.[17]

According to the recent ab initio calculations,[18] OSN is lower in energy than SNO by about 3 kcal mol^{-1}. Experimentally, SNO has been identified by IR spectroscopy during the $\lambda = 121.6$ nm photolysis of HNSO[19] and the reaction between sulfur atoms with NO in solid noble-gas matrices.[20] In contrast, for the more stable OSN, the generally recognized[18,21] experimental evidence is the single IR band at 1195 cm^{-1} which was detected during the 121.6 nm photolysis of Ar-matrix-isolated HNSO.[19] Despite the IR frequency being close to the predicted value of 1209.2 cm^{-1},[18] the large discrepancy of the ^{15}N isotope shift between the measured value (9.4 cm^{-1}) and the prediction (5.3 cm^{-1}) casts some doubt on the identification. Moreover, little evidence was obtained for conversion from OSN into SNO upon irradiation at wavelengths greater than 200 nm.[19]

---

[*] Z. Wu, D. Q. Li, H. M. Li, B. F. Zhu, H. L. Sun, Prof. Dr. X. Q. Zeng
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
Homepage: http://web.suda.edu.cn/xqzeng/index.html
Prof. Dr. J. S. Francisco
Department of Chemistry, Purdue University
West Lafayette, IN 47907 (USA)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201510105.

Herein, the thermal decomposition of gaseous $CF_3S(O)N_3$[22] is studied and two novel sulfur–nitrogen-containing intermediates, sulfinylnitrene $CF_3S(O)N$ and iminyl radical OSN, are produced and unambiguously identified for the first time.

The FVP of $CF_3S(O)N_3$ diluted in neon (circa 1:1000) is performed by passing the mixture through a heated Al_2O_3 furnace followed by immediate deposition onto the cryogenic Au-plated copper matrix support (for experimental details, see the Supporting Information). The matrix-solation IR spectrum of the pyrolysis products at 350 °C is shown in the middle trace in Figure 1 (the full spectrum is given in Figure S1 in the Supporting Information). Comparing to the spectrum of $CF_3S(O)N_3$ (Figure 1, lower trace), the azide decomposes almost completely at this temperature. In addition to CF_3 (species c; 1252.7 and 1086.3 cm^{-1}) and SO_2 (species d; 1358.6 cm^{-1}),[15] another species (b) exhibiting IR bands at 1452.7, 1261.1, 1219.3, 1141.4, 1059.2, and 755.6 cm^{-1} is produced (Figure 1, middle trace). When the pyrolysis temperature increases to 450 °C, no azide is left and the yields of SO_2 and CF_3 are significantly enhanced at the expense of fragment b (Figure 1, top trace).

To aid the assignment, the same pyrolysis experiments are carried out for a 1:1 mixture of $CF_3S(O)^{15}NNN$ and $CF_3S(O)NN^{15}N$. In the corresponding IR spectrum, distinct doublets are detected for the IR bands at 1452.7, 1141.4, and 1059.2 cm^{-1} (Figure S2), which strongly support their assignment to the sulfinylnitrene $CF_3S(O)N$. This assignment is confirmed by the agreement of the detected IR frequencies with theoretical calculations, carried out at the B3LYP/6-311 + G(3df) level of theory, for the lowest-energy singlet state (Table 1). According to the calculations, the singlet nitrene has two dipolar oxathiazyne (Scheme 1, II) and oxathiazirine resonance structures (III). Structure III is significantly higher in energy than structure II ($\Delta E = 39.8$ kcal mol^{-1}) and is higher than the triplet state by 7.5 kcal mol^{-1} at the CBS-QB3 level (Figure S3).

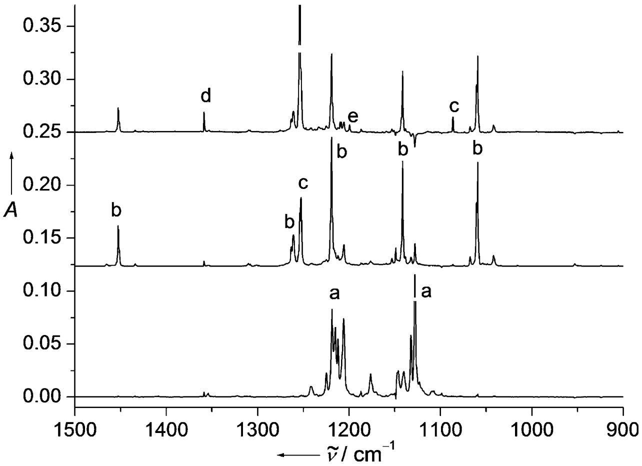


Figure 1. Matrix IR spectra of $CF_3S(O)N_3$ (lower trace), the FVP products of $CF_3S(O)N_3$ at 350 °C (middle trace), and the FVP products of $CF_3S(O)N_3$ at 450 °C (upper trace). The IR bands of a) $CF_3S(O)N_3$, b) $CF_3S(O)N$, c) CF_3, d) SO_2, and e) OSN are labelled.

The two bands at 1452.7 and 1141.4 cm^{-1} are attributed to the antisymmetric and symmetric stretches of the NSO group, and the latter is strongly coupled with the in-phase symmetric CF_3 stretch (Table 1). The out-of-phase coupled stretching vibration appears at 1059.2 cm^{-1}. The two antisymmetric CF_3 stretches occur at 1261.1 and 1219.3 cm^{-1}. It is worth to note that the almost equally large isotope shifts $\Delta\nu(^{14/15}N)$ (18.1 cm^{-1}) and $\Delta\nu(^{32/34}S)$ (18.2 cm^{-1}) for the antisymmetric NSO stretch agree with a formal N=S double bond in the oxathiazyne-like sulfinylnitrene, and the frequency is much higher than those of free SO (1138.7 cm^{-1})[23] and NS (1209.4 cm^{-1}).[24]

As is shown in Figure 1, the increase of the pyrolysis temperature from 350 to 450 °C facilitates further dissociation of $CF_3S(O)N$. However, in addition to CF_3 the IR bands for the other pyrolysis products are fairly weak (Figure 1). Therefore, the temperature was increased to about 600 °C. The corresponding IR spectrum (Figure S4) shows the survival of $CF_3S(O)N$, together with CF_3, SO_2, F_2CO (species f; 1941.1, 1909.6, 1237.4, and 968.0 cm^{-1}),[25] and SO_3 (band h; 1390.6 cm^{-1}).[26] Importantly, another nitrogen-containing species (e) having two IR bands at 1199.3 and 995.3 cm^{-1} becomes distinguishable, especially by the distinct ^{15}N isotope shifts of 5.6 and 20.5 cm^{-1}, respectively.

To distinguish the complex pyrolysis products, the matrices are subsequently irradiated using a $\lambda = 193$ nm ArF excimer laser. The resulting IR difference spectra reflecting the changes are shown in Figure 2. Upon irradiation, the IR bands of $CF_3S(O)N$ (b) and OSN (e) are completely destroyed, and those of CF_3 (c), SO_2 (d), and SO_3 (h) are partially depleted. As a result, F_2CO (f), SNO (i), and unidentified species with weaker IR bands are produced.

Table 1: Calculated and experimental IR frequencies (ν; cm^{-1}) and isotopic shifts ($\Delta\nu$; cm^{-1}) for the fundamental vibrations of $CF_3S(O)N$.

ν_{calc}[a]			ν_{exp}[b]		$\Delta\nu$ ($^{14/15}N$)[c]		$\Delta\nu$ ($^{32/34}S$)[d]		assignment[e]	
singlet II	singlet III	triplet	Ar matrix	Ne matrix	calc	exp	calc	exp		
1486 (75)	1240 (211)	1222 (274)	1445.7	1452.7	20.0	18.1	19.2	18.2	ν_1	$\nu_{asym}(NSO)$
1244 (235)	1160 (258)	1203 (272)	1257.7	1261.1	0.1	< 0.5	0.1	< 0.5	ν_{11}	$\nu_{asym}(CF_3)$
1204 (292)	1109 (270)	1153 (20)	1218.1	1219.3	0	< 0.5	0	< 0.5	ν_2	$\nu_{asym}(CF_3)$
1145 (82)	1023 (58)	1061 (370)	1137.2	1141.4	8.0	4.5	4.3	3.1	ν_3	$\nu_{sym}(CF_3) + \nu_{sym}(NSO)$
1055 (312)	823 (7)	738 (19)	1055.0	1059.2	4.0	7.1	0.9	< 0.5	ν_4	$\nu_{sym}(CF_3) + \nu(CS)$
753 (19)	743 (4)	656 (26)	750.1	755.6	0.2	< 0.5	0.4	< 0.5	ν_5	$\delta_{sym}(CF_3)$

[a] Harmonic frequencies calculated at the DFT B3LYP/6-311 + G(3df) level of theory, calculated IR intensities (km mol^{-1}) are given in parenthesis. The calculated molecular structures are given in Figure S3. [b] Band positions of the most intense matrix sites in neon and argon at 2.7 K. [c] ^{15}N isotope shifts. [d] ^{34}S isotope shifts. [e] Tentative assignments based on the calculated vibrational displacement vectors.

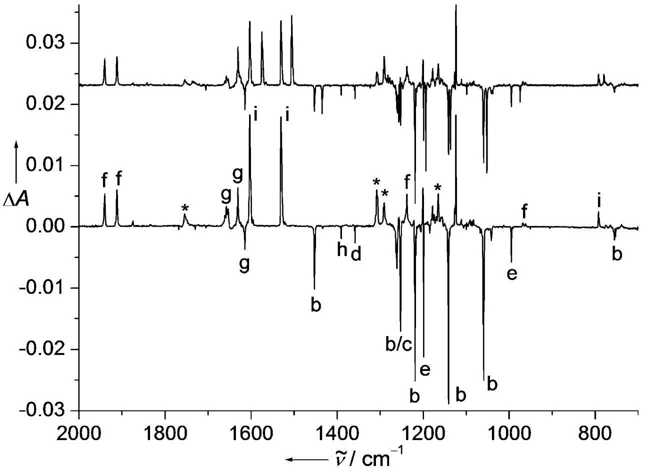


Figure 2. IR difference spectra showing the photoinduced ($\lambda = 193$ nm) changes of matrix-isolated FVP products of $CF_3S(O)N_3$ at about 600 °C (lower trace) and the photoinduced ($\lambda = 193$ nm) changes of matrix-isolated FVP products of 1:1 mixture of $CF_3S(O)^{15}NNN$ and $CF_3S(O)NN^{15}N$ (upper trace). The IR bands of b) $CF_3S(O)N$, c) CF_3, d) SO_2, e) OSN, f) F_2CO, g) H_2O, h) SO_3, and i) SNO are labelled. The bands attributable to unknown species are labelled with asterisks.

The identification of SNO (i)[20] is confirmed by the IR frequencies 1603.6 (ν_1), 1530.5 ($2\nu_3$), and 792.3 cm^{-1} (ν_3) with ^{15}N isotope shifts of 28.7, 24.6, and 12.5 cm^{-1}, respectively. As the most likely precursor of SNO, its isomer OSN is predicted to have two stretching vibrations at 1209.2 (ν_1) and 1010.7 cm^{-1} (ν_2) with ^{15}N isotope shifts of 5.3 and 21.0 cm^{-1}, respectively.[18] The excellent agreement of these data with the values measured for species e (Table 2) casts no doubt on its assignment to OSN. The remaining fundamental IR band for the OSN bending mode, predicted to be 302.1 cm^{-1},[18] was not detected within the experimental spectral range (4000–650 cm^{-1}) available in this study. As aided by the calculations,[18] the ^{34}S isotope shifts derived from the naturally abundant ^{34}S are obtained (Table 2).

According to the theoretical study,[18] the first two IR fundamentals can be best described as symmetric (ν_1) and antisymmetric (ν_2) stretching modes of OSN. Their difference is 203.9 cm^{-1}, which is very close to that of SO_2 (205.4 cm^{-1}), an analogue with one additional electron. The frequency of 1199.3 cm^{-1} measured in solid neon for ν_1 coincides with the previously detected band (1195 cm^{-1}) during the photolysis of HNSO in solid argon.[19] However, the unexpectedly large ^{15}N isotope shift of 9.4 cm^{-1} reported previously renders this early assignment[19] to OSN questionable. To check the influence of noble gas matrices on the band position, the FVP of $CF_3S(O)N_3$ is repeated by using argon as the host gas. Under these conditions, the IR band for ν_1 changes into a doublet at 1197.1 and 1193.6 cm^{-1}, with the splitting probably caused by different matrix surroundings. Therefore, the band at 1195 cm^{-1} detected in the earlier study[19] seems unlikely to be associated with OSN.

Table 2: Calculated and experimental IR frequencies and isotopic shifts (cm^{-1}) for the OSN species.

ν			$\Delta\nu(^{14/15}N)$		$\Delta\nu(^{32/34}S)$	
calc[a]	Ne (exp)[b]	Ar (exp)[c]	calc[a]	exp[b]	calc[a]	exp[b]
1209.2	1199.3	1197.1/1193.6	5.3	5.6	14.6	14.2
1010.7	995.4	995.1/990.9	21.0	20.5	4.0	3.7

[a] Anharmonic frequencies and isotope shifts calculated by the reported CcCR QFF method.[18] [b] Band positions and isotope shifts detected in a neon matrix at 2.7 K. [c] Band positions detected in an argon matrix at 2.7 K.

In addition to the depletion of OSN (species e), the nitrene $CF_3S(O)N$ (species b) is also destroyed upon irradiation with the $\lambda = 193$ nm laser (Figure 2). However, neither its Curtius-like rearrangement product CF_3NSO[27] nor isomeric CF_3SNO[28] could be identified among the photolysis products. Interestingly, traces of NO are identifiable by the presence of the IR band at 1875.2 cm^{-1} ($\Delta\nu(^{14/15}N) =$ 33.2 cm^{-1}),[29] which might be produced from the photolysis of SNO. The study on the complex photochemistry of $CF_3S(O)N$ in noble-gas matrices is currently underway.

To account for the formation of $CF_3S(O)N$ and OSN from the thermal decomposition of $CF_3S(O)N_3$, quantum chemical calculations on the decomposition pathways were carried out and the results are depicted in Figure 3. Both *syn* and *anti* conformers of $CF_3S(O)N_3$ (Figure S5) undergo stepwise decomposition via the nitrene $CF_3S(O)N$. This decomposition pathway is in sharp contrast to carbonyl azides, for which usually the *syn* and *anti* conformers prefer concerted and stepwise decomposition pathways, respectively.[30] The activation barrier for the decomposition of *syn*-$CF_3S(O)N_3$ (22.3 kcal mol^{-1}; CBS-QB3 level of theory) is comparable to that for the favorable concerted decomposition of *syn*-$HC(O)N_3$ (22.3 kcal mol^{-1}; CCSD(F12)(T) level of theory) to HNCO and N_2,[30] with both compounds quickly liberating N_2 at room temperature.

For the initially generated sulfinylnitrene $CF_3S(O)N$, the barrier of the Curtius-like rearrangement[31] to CF_3NSO is 32.7 kcal mol^{-1}, greater than the C–S bond dissociation energy (24.6 kcal mol^{-1}). This is consistent with the observation that $CF_3S(O)N$ is thermally more stable than the azide precursor, and its dissociation furnishes CF_3 and OSN

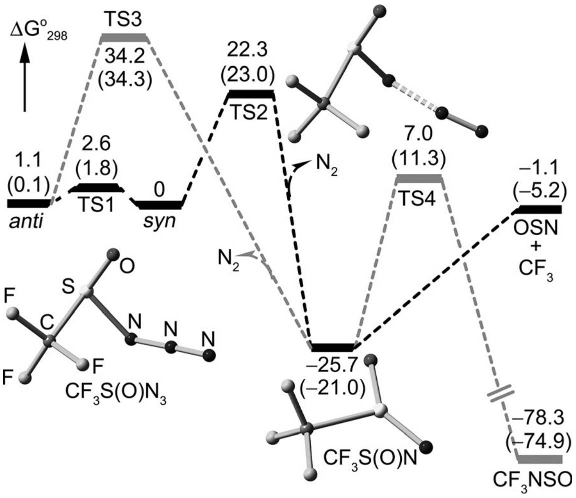


Figure 3. Calculated energy profile (kcal mol^{-1}) for the decomposition of $CF_3S(O)N_3$ at the CBS-QB3 and B3LYP/6-311+G(3df) (in parentheses) levels.

radicals. The absence of isomeric SNO under the pyrolysis conditions is also consistent with the predicted extremely large activation barrier (62 kcal mol^{-1}, B3LYP/6-311 + G*)[32] from OSN to SNO.

In conclusion, we have presented the first experimental evidence for the generation of a sulfinylnitrene CF$_3$S(O)N and the sulfinyliminyl radical OSN during the flash vacuum pyrolysis of CF$_3$S(O)N$_3$. Initially, the azide eliminates N$_2$ and forms CF$_3$S(O)N at 350 °C. This nitrene prefers an oxathiazyne rather than oxathiazirine-like structure, as indicated by the measured IR spectrum. Further fragmentation of this nitrene at about 600 °C offers unique access to OSN. The unambiguous identification of OSN in the present study renders the previous assignment of the IR band at 1209.4 cm^{-1} to this species questionable. The facile gas-phase production of these two novel small sulfur–nitrogen compounds should stimulate further studies on their structure and reactivity.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (21372173, 21422304), the Beijing National Laboratory for Molecular Sciences (20140128), and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD). The authors thank Dr. Helmut Beckers for helpful discussion.

Keywords: azides · density functional calculations · IR spectroscopy · matrix isolation · nitrenes

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 1507 – 1510
Angew. Chem. **2016**, *128*, 1529 – 1532

---

[1] a) *Nitrenes and Nitrenium Ions (Wiley Series of Reactive Intermediates in Chemistry and Biology)*, *Vol. 6th* (Eds.: D. E. Falvey, A. D. Gudmundsdottir), Wiley, New Jersey, **2013**; b) *Reactive Intermediate Chemistry* (Eds.: R. A. Moss, M. S. Platz, M. J. Jones), Wiley-Interscience, New Jersey, **2004**; c) "The Study of Nitrenes by Theoretical Methods": N. P. Gritsan, M. S. Platz, W. T. Borden in *Theoretical Methods in Photochemistry* (Eds.: A. Kutateladze); Taylor and Francis, Boca Raton, **2005**; d) E. F. V. Scriven, *Azides and Nitrenes*; *Reactivity and Utility*, Academic Press, New York, **1984**.

[2] For recent examples, see: a) S. K. Sarkar, A. Sawai, K. Kanahara, C. Wentrup, M. Abe, A. D. Gudmundsdottir, *J. Am. Chem. Soc.* **2015**, *137*, 4207 – 4214; b) M. Winkler, W. Sander, *Acc. Chem. Res.* **2014**, *47*, 31 – 44; c) C. Wentrup, *Acc. Chem. Res.* **2011**, *44*, 393 – 404.

[3] J. Kubicki, Y. Zhang, S. Vyas, G. Burdzinski, H. L. Luk, J. Wang, J. Xue, H.-L. Peng, E. A. Pritchina, M. Sliwa, G. Buntinx, N. P. Gritsan, C. M. Hadad, M. S. Platz, *J. Am. Chem. Soc.* **2011**, *133*, 9751 – 9761, and references therein.

[4] S. Vyas, S. Muthukrishnan, J. Kubicki, R. D. McCulla, G. Burdzinski, M. Sliwa, M. S. Platz, C. M. Hadad, *J. Am. Chem. Soc.* **2010**, *132*, 16796 – 16804, and references therein.

[5] X. Q. Zeng, H. Beckers, H. Willner, *J. Am. Chem. Soc.* **2013**, *135*, 2096 – 2099, and references therein.

[6] a) T. Pasinszki, G. Bazsó, M. Krebsz, G. Tarczay, *Phys. Chem. Chem. Phys.* **2009**, *11*, 9458 – 9467; b) Y. Liu, A. S. Evans, J. P. Toscano, *Phys. Chem. Chem. Phys.* **2012**, *14*, 10438 – 10444.

[7] a) H. M. Li, Z. Wu, D. Q. Li, X. Q. Zeng, H. Beckers, J. S. Francisco, *J. Am. Chem. Soc.* **2015**, *137*, 10942 – 10945; b) G. Bertrand, J.-P. Majoral, A. Baceiredo, *Acc. Chem. Res.* **1986**, *19*, 17 – 23.

[8] a) T. Pasinszki, M. Krebsz, G. Tarczay, C. Wentrup, *J. Org. Chem.* **2013**, *78*, 11985 – 11991; b) J. H. Davis, W. A. Goddard III, *J. Am. Chem. Soc.* **1977**, *99*, 7111 – 7121.

[9] P. A. Denis, O. N. Ventura, H. T. Mai, M. T. Nguyen, *J. Phys. Chem. A* **2004**, *108*, 5073 – 5080.

[10] a) F. Dielmann, O. Back, M. Henry-Ellinger, P. Jerabek, G. Frenking, G. Bertrand, *Science* **2012**, *337*, 1526 – 1528; b) X. Q. Zeng, H. Beckers, H. Willner, *Angew. Chem. Int. Ed.* **2009**, *48*, 4828 – 4831; *Angew. Chem.* **2009**, *121*, 4922 – 4925.

[11] a) A. Igau, H. Grützmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1988**, *110*, 6463 – 6466; b) A. Baceiredo, G. Bertrand, G. Sicard, *J. Am. Chem. Soc.* **1985**, *107*, 4781 – 4783; c) G. Sicard, H. Grützmacher, A. Baceiredo, J. Fischer, G. Bertrand, *J. Org. Chem.* **1989**, *54*, 4426 – 4430.

[12] a) T. J. Maricich, V. L. Hoffman, *J. Am. Chem. Soc.* **1974**, *96*, 7770 – 7781; b) T. J. Maricich, C. N. Angeletakis, *J. Org. Chem.* **1984**, *49*, 1931 – 1934; c) T. J. Maricich, C. N. Angeletakis, R. Mjanger, *J. Org. Chem.* **1984**, *49*, 1928 – 1931; d) T. J. Maricich, S. Madhusoodanan, *Tetrahedron Lett.* **1977**, *18*, 983 – 986.

[13] X. Q. Zeng, H. Beckers, H. Willner, J. F. Stanton, *Angew. Chem. Int. Ed.* **2011**, *50*, 1720 – 1723; *Angew. Chem.* **2011**, *123*, 1758 – 1761.

[14] X. Q. Zeng, H. Beckers, H. Willner, *J. Am. Chem. Soc.* **2011**, *133*, 20696 – 20699, and references therein.

[15] X. Q. Zeng, H. Beckers, H. Willner, *Angew. Chem. Int. Ed.* **2013**, *52*, 7981 – 7984; *Angew. Chem.* **2013**, *125*, 8139 – 8142.

[16] a) M. Méndez, J. S. Francisco, D. A. Dixon, *Chem. Eur. J.* **2014**, *20*, 10231 – 10235; b) O. Yazidi, A. B. Houria, J. S. Francisco, M. Hochlaf, *J. Chem. Phys.* **2013**, *138*, 104318.

[17] T. Chivers in *A Guide to Chalcogen-Nitrogen Chemistry*, World Scientific, London, **2005**.

[18] R. C. Fortenberry, J. S. Francisco, *J. Chem. Phys.* **2015**, *143*, 084308.

[19] P. O. Tchir, R. D. Spratley, *Can. J. Chem.* **1975**, *53*, 2331 – 2336.

[20] a) L. Andrews, P. Hassanzadeh, G. D. Brabson, A. Citra, *J. Phys. Chem.* **1996**, *100*, 8273 – 8279; b) M. Bahou, Y.-P. Lee, *J. Chem. Phys.* **2001**, *115*, 10694 – 10700.

[21] a) R. N. Perutz, *Chem. Rev.* **1985**, *85*, 97 – 127; b) NIST Chemistry Webbook: http://webbook.nist.gov/chemistry/.

[22] T. Bechtold, A. Eingelbrecht, *J. Fluorine Chem.* **1982**, *19*, 379 – 402.

[23] X. Q. Zeng, H. Beckers, P. Neuhaus, D. Grote, W. Sander, *Z. Anorg. Allg. Chem.* **2012**, *638*, 526 – 533.

[24] P. Hassanzadeh, L. Andrews, *J. Am. Chem. Soc.* **1992**, *114*, 83 – 91.

[25] H. F. Bettinger, H. Peng, *J. Phys. Chem. A* **2005**, *109*, 23218 – 23224.

[26] H. Chaabouni, L. Schriver-Mazzuoli, A. Schriver, *J. Phys. Chem. A* **2000**, *104*, 3498 – 3507.

[27] A. F. Antognini, H. Oberhammer, E. H. Cutin, N. L. Robles, *J. Mol. Struct.* **2012**, *1023*, 75 – 80.

[28] J. (Banus) Mason, *J. Chem. Soc.* **1969**, 1587 – 1592.

[29] M. E. Jacox, W. E. Thimpson, *J. Chem. Phys.* **2008**, *129*, 204306.

[30] K. Banert, C. Berndt, M. Hagedorn, H. Liu, T. Anacker, J. Friedrich, G. Rauhut, *Angew. Chem. Int. Ed.* **2012**, *51*, 4718 – 4721; *Angew. Chem.* **2012**, *124*, 4796 – 4800.

[31] T. Curtius, *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 3023 – 3033.

[32] L. X. Sun, Y. X. Bu, S. H. Yan, *Chem. Phys. Lett.* **2003**, *370*, 616 – 624.

Received: October 30, 2015