Elusive Isomers

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Isomers of Disulfur Dinitride, S_2N_2**

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Abstract: *UV photolysis ($\lambda = 248$ or 255 nm) of cyclic S_2N_2 isolated in solid argon matrices yields two open-shell S_2N_2 isomers, trans SNSN ($^3A''$) and cis SNSN ($^3A''$), as well as a closed-shell C_{2v} dimer $(SN)_2$ ($^1A_1$). These novel isomers have been characterized by their IR spectra and mutual photo-interconversion reactions. Quantum chemical calculations support the experimental results and also provide insight into the complex potential energy surface of S_2N_2.*

Binary sulfur–nitrogen compounds are of broad interest in structural and synthetic inorganic chemistry as well as in material science.[1] The key compound of the rich sulfur–nitrogen chemistry is tetrasulfur tetranitride, S_4N_4.[2,3] It was discovered in 1835,[2] and has been the subject of extensive studies.[3] By thermal cracking of gaseous S_4N_4 on silver wool, the more challenging disulfur dinitride, S_2N_2, was obtained.[4] Solid S_2N_2 was found to undergo thermally or photolytically induced polymerization at low temperature to form polysulfur nitride, $(SN)_x$.[5] The outstanding properties of S_2N_2 are of ongoing interest in inorganic chemistry.[6]

Unlike the N–N bonded N_2O_2,[7] the homologous disulfur dinitride, S_2N_2, consists in a planar SNSN ring structure of D_{2h} symmetry (1,3,2,4-dithiadiazete).[6a,8] However, beyond this planar ring structure, theoretical studies predict the existence of several isomers on both the lowest singlet and triplet potential energy surfaces (PES) of S_2N_2.[9] Among them, linear SNNS ($^1\Sigma_g^+$) and planar cyclic 1,2,3,4-dithiadiazete (C_{2v}) with pairwise N=N and S–S bonds were found to be even lower in energy than the SNSN D_{2h} ring structure.[9a,c] Trigonal planar (Y-shaped) isomers, planar chains, and puckered four-membered rings represent alternative higher-energy minima on both the singlet and the triplet PES of S_2N_2. Some of these structures have already been established for isoelectronic tetraatomic molecules with 22 valence electrons, such as C_2F_2 (linear and planar Y-shaped),[10a,b] N_2O_2 (planar *cis* chain),[7] CO_3 (planar Y-shaped),[10c] and P_4^{2-} (square planar).[10d] Of particular interest with regard to the polymerization of S_2N_2 are proposed intermediate biradicals with *cis*-bent SNSN structures.[9]

Although S_2N_2 (D_{2h}) is metastable with respect to N_2 and S_2 and even explodes violently when heated higher than 30 °C,[4,8a] its dissociation into two SN radicals was found to be hindered by a barrier of about 200 kJ mol^{-1}.[9] On the other hand, the lowest triplet state was predicted to be about 170 kJ mol^{-1} above the singlet ground state.[9b,c]

Despite the long history and numerous studies on S_2N_2, it is surprising that only the D_{2h} ring structure has been up to now firmly established experimentally. In an early study, Hassanzadeh and Andrews reported the matrix isolation of binary sulfur–nitrogen species produced in a sulfur/nitrogen/argon vapor discharge.[11] Although cyclic S_2N_2 (D_{2h}) was not observed under these conditions, formation of an acyclic NSSN isomer assigned to an IR band at 1167.4 cm^{-1} in solid argon was claimed.[11] Searching for such elusive S_2N_2 isomers, we describe herein the ring-opening UV photolysis of matrix-isolated S_2N_2 (D_{2h}) at which novel open-shell S_2N_2 isomers have been established. The identity of our new S_2N_2 species has been unambiguously proved by their vibrational spectra in ^{15}N-labeling experiments, in mutual photo-isomerization reactions, and by quantum-chemical calculations.

For the matrix-isolation experiments, S_2N_2 (ca. 5 mg) was transferred in vacuo into a small U-trap and placed in front of the matrix support. A gas stream of Ar (2 mmol h^{-1}) passed over the cold sample (−15 °C), and the resulting mixture was deposited onto the matrix support at 16 K in a high vacuum (see the Supporting Information for details). UV irradiation into the π–π* electronic band of S_2N_2[12] using two different light sources of $\lambda_{max} = 255$ and 248 nm strongly depleted its IR bands. Several new IR bands appeared in the region 1150–1250 cm^{-1} that are characteristic for terminal S=N stretching vibrations (Supporting Information, Figures S1 and S2).

Several carriers bearing terminal S=N bonds are considered and they are among those depicted in Figure 1. The acyclic isomers may adopt either *cis* or *trans* planar configuration and might be trapped in their lowest singlet or triplet states. Planar bent isomers with alternate SNSN structures (b, c) are probably produced by photoinduced cleavage of one S–N bond of cyclic S_2N_2 (a). In contrast, formation of NSSN structures (h, i) needs cleavage of two S–N bonds, or recombination of two SN radicals. In any case, all four

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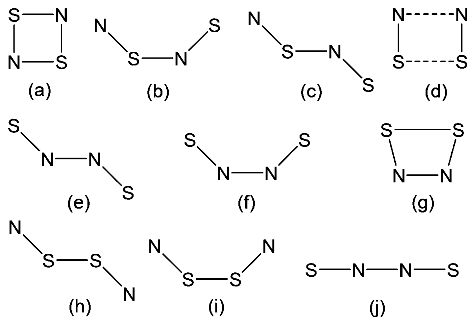


Figure 1. Planar cyclic and planar acyclic isomers of S_2N_2.

atoms of the precursor S_2N_2 (a) should stay within the matrix cage under the photolysis. In accord with this expectation, the absorption that is due to the thiazyl (SN) monomer in solid Ar, previously attributed to an IR band at 1209.4 cm^{-1},[11] was not detected among the photolysis products. Searching for two weakly interacting SN radicals at both B3LYP/6-311+G (3df) and CCSD/cc-pVTZ levels, we found a C_{2v} dimer (d) as another candidate that exhibits S=N stretching frequencies.

The assignment of the isomers (b), (c), and (d) in the IR spectra in Figure 2 and 3 was confirmed by using a $^{14/15}N$-labeled precursor (1:1). The two bands at 1251.6 and 1226.1 cm^{-1} reveal distinct 1:1 doublet patterns, and their $^{14/15}N$ isotope shifts of 28.8 and 27.9 cm^{-1}, respectively, are similar to that reported for the SN monomer isolated in solid Ar ($\Delta\nu(^{14/15}N) = 28.1\ cm^{-1}$).[11] Such isotopic patterns suggest the formation of SNSN chain isomers (b,c) bearing a single terminal S=N bond. The photoinduced interconversion between the initially formed S_2N_2 isomers (Figure 2) confirms the formation of the bent SNSN species b and c and enables the unambiguous assignment of several far-IR bands (Figure 3) as well as two combination bands. The agreement between experimental and calculated frequencies listed in Table 1 is compelling (see also the Supporting Information, Tables S1 and S2).

Both bent SNSN isomers (b) and (c) are depleted by visible light irradiation of $\lambda_{max} \approx 520$ nm, producing the weakly bound SN dimer (d), $(SN)_2$ ($^1A_1$, C_{2v}; Figure 2, bottom trace). Re-formation of species (b) and (c) at the expense of (d) was achieved by irradiation with light of $\lambda \geq 320$ nm (Figure 2, upper trace). From these spectra it is

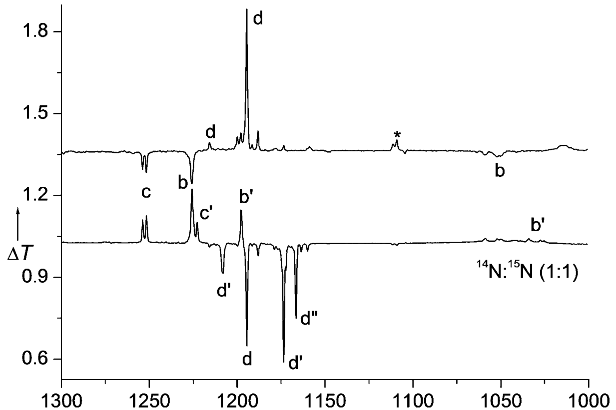


Figure 2. IR difference spectra: Upper trace: conversion of $(SN)_2$ (d, C_{2v}, $^1A_1$) into *cis* (b, C_s, $^3A''$) and *trans* SNSN (c, C_s, $^3A''$) by irradiation with UV light of $\lambda \geq 320$ nm (5 min). Lower trace: reverse conversion of ^{15}N-labeled ($^{14}N:^{15}N = 1:1$) *cis* (b) and *trans* SNSN (c) to $(SN)_2$ (d) under irradiation with green light ($\lambda_{max} \approx 520$ nm, 10 min). Primed symbols refer to ^{15}N enriched isotopologues. A band of an unknown species is labeled by an asterisk.

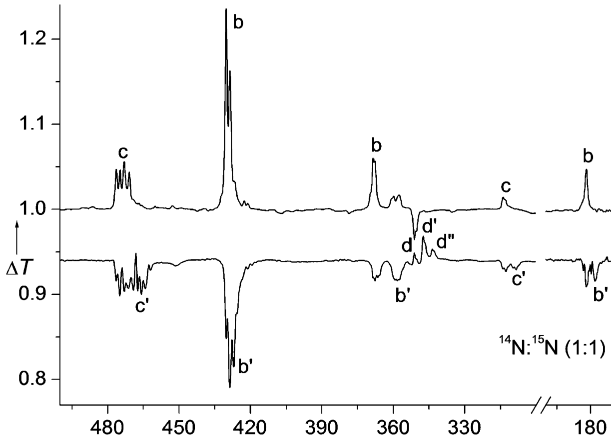


Figure 3. Far-IR difference spectra: Upper trace: conversion from *cis* (b, C_s, $^3A''$) and *trans* SNSN (c, C_s, $^3A''$) into $(SN)_2$ (d, C_{2v}, $^1A_1$) by irradiation with light of $\lambda_{max} \approx 365$ nm (20 min), Lower trace: reverse conversion of ^{15}N-labeled ($^{14}N:^{15}N = 1:1$) $(SN)_2$ (d) to *cis* (b) and *trans* SNSN (c) under irradiation of UV light ($\lambda \geq 305$ nm, 10 min). Primed symbols refer to ^{15}N enriched isotopologues.

Table 1: Calculated and observed IR frequencies and isotope shifts $\Delta\nu(^{15}N)$ [cm^{-1}] of S_2N_2 isomers.

cis-SNSN (b, C_s, $^3A''$)			*trans*-SNSN (c, C_s, $^3A''$)			$(SN)_2$ (d, C_{2v}, $^1A_1$)		
Calculated[a]	Observed[b]		Calculated[a]	Observed[b]		Calculated[a]	Observed[b]	
ν_i	ν_i	$\Delta\nu(^{15}N)$[b]	ν_i	ν_i	$\Delta\nu(^{15}N)$[b]	ν_i	ν_i	$\Delta\nu(^{15}N)$[b]
1654.2 (vw)[d]	30.1		1726.7 (vw)[e]					
1231 (53)	1226.1 (s)	27.9	1261 (61)	1251.6 (m)	28.8	1250 (6)	1215.8 (vw)	7.4, (27.9)[c]
1048 (5)	1059.0 (w)	25.1	1036 (3)			1200 (259)	1194.5 (s)	21.1, 28.0
416 (73)	430.2 (s)	1.6	451 (108)	473.2 (m)	7.4	368 (4)	351.1 (vw)	3.7, 8.1
338 (52)	368.5 (m)	10.3	295 (24)	312.7 (w)	4.2	234 (<1)		
183 (14)	181.9 (m)	4.0	175 (1)			160 (0)		
156 (2)			102 (<1)			116 (4)		

[a] Calculated IR frequencies (scaled by a factor of 0.9679) and intensities (in parentheses, in $km\,mol^{-1}$) at the B3LYP/6-311+G(3df) level. [b] Solid Ar matrix, 16 K, relative intensities: s strong, m medium, w weak, vw very weak, $\Delta\nu(^{15}N)$ relative to the natural isotopologue (for comparison with calculated values, see the Supporting Information, Tables S1–S3). [c] Tentative assignment due to overlap with a matrix site of the natural isotopomer. [d] Combination band ($1226.1 + 430.2 = 1656.3\ cm^{-1}$). [e] Combination band ($1251.6 + 473.2 = 1724.8\ cm^{-1}$).

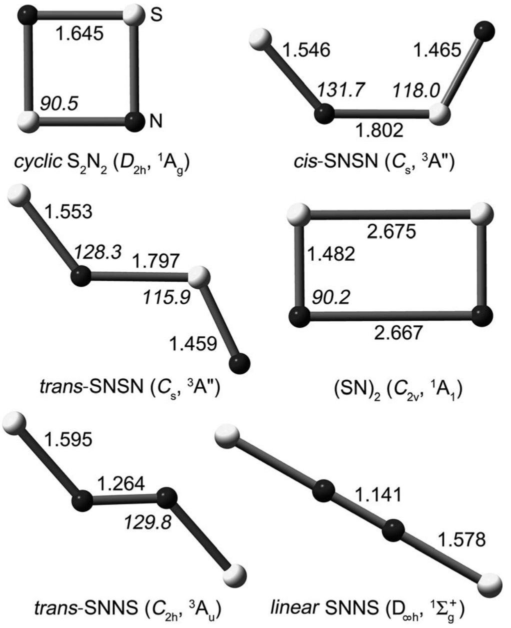
apparent that carrier (d) shows two S=N bands at 1215.8 and 1194.5 cm^{-1} and the $^{14/15}$N mixed sample produced three isotopologues of (d) (Supporting Information, Table S3).

The presence of two coupled S=N stretching modes supports the assignment of the SN dimer (d), and rules out a *trans* S–S bonded species (h) (C_{2h}, Figure 1). Also the vibrational splitting of 21.3 cm^{-1} for the in- and out-of-phase S=N modes of (d) is much smaller than that predicted for the S–S bonded species (i) (138 cm^{-1}, *cis* NSSN, $^3B_1$; Supporting Information, Table S4). The averaged frequencies of the two S=N modes of (d) (1205.1 cm^{-1}) and their $^{14/15}$N isotopic shifts are close to those of the SN monomer (1209.4 cm^{-1}, $\Delta\nu(^{14/15}N) = 28.1$ cm^{-1}),[11] indicating only small perturbations to the two SN moieties. Within the instrumental frequency range available to this study (> 180 cm^{-1}) and in accord with calculated vibrational data (Table 1), one additional weak feature is attributed to this dimer in the far-IR spectrum at 351.1 cm^{-1} (Figure 3).

The photochemistry of the new S_2N_2 isomers provides insight into their electronic configuration. Time-dependent (TD)-DFT calculations for the triplet isomers generally reveal electronic transitions in the near UV/Vis region $\lambda >$ 350 nm, while the lowest-energy π–π* transitions of the singlet species are predicted in the region $\lambda < 350$ nm (Supporting Information, Table S5). Thus, the photochemical behavior of the bent SNSN photoproducts discloses their open-shell nature, for example, triplet *cis* SNSN ($^3A''$, b), and *trans* SNSN ($^3A''$, c). This assignment is consistent with quantum chemical calculations,[9c] which revealed triplet ground states for the planar bent SNSN isomers (b) and (c), while their lowest singlet states were found to be energetically close to the NS ($^2\Pi$) + NS ($^2\Pi$) dissociation limit.[9]

Secondary products obtained after near-UV (280 nm $\leq \lambda \leq$ 405 nm) photolysis of matrix-isolated S_2N_2 are N_2S ($C_{\infty v}$, 2040.2 cm^{-1}, $\Delta\nu(^{14/15}N) = 31.1$, 36.2, and 67.8 cm^{-1})[13] and likely S atoms or $N_2 + S_2$ (IR-inactive). While IR bands of bent NS_2 (C_{2v}),[11] previously observed in an Ar matrix at 1499.7 cm^{-1} and 1225.2 cm^{-1}, were not found in our study, N_2S ($C_{\infty v}$) could be formed through the photodecomposition of hitherto unknown N–N bonded S_2N_2 isomers. N–N bonded isomers bearing two equivalent N-atoms should provide a readily recognizable 1:2:1 isotope pattern in experiments using ^{15}N-enriched samples (^{14}N:$^{15}N = 1$:1). Such an isotope pattern has indeed been observed for a single absorption in the S–N bond stretching region at 909.1 cm^{-1} ($\Delta\nu(^{14/15}N) =$ 10.9 and 20.9 cm^{-1}) after irradiation of the bent SNSN species using a green LED light ($\lambda_{max} \approx 520$ nm; Supporting Information, Figure S3). Near-UV LED ($\lambda_{max} \approx 405$ nm) photolysis caused depletion of this band and formation of N_2S ($C_{\infty v}$). DFT calculations predict the formation of triplet *trans* SNNS (C_{2h}, ^3A_u) from the bent SNSN species via a cyclic transition state lower in energy (178 kJ mol^{-1}) than the energy utilized in the radiation (520 nm = 230 kJ mol^{-1}; Figure S4 in the Supporting Information). Calculated IR data for this N–N bonded isomer fits well to the appearance of a single fundamental IR band at 889 cm^{-1} ($\Delta\nu(^{14/15}N) = 10.8$ and 20.8 cm^{-1}) within the spectral range available to this study (Supporting Information, Table S6), and its predicted electronic transitions (Supporting Information, Table S5) are consistent with the observed photodegradation of the weak band at 909.1 cm^{-1}. Thus, we are tempted to assign this feature to *trans* SNNS (C_{2h}, ^3A_u).

Calculated structures for the species of most interest in this work are summarized in Figure 4. We note that DFT B3LYP calculations put the closed-shell linear species SNNS ($D_{\infty h}$, $^1\Sigma_g^+$) at the global minimum of S_2N_2 (Supporting Information, Table S7), while inclusion of electron correlation at the CCSD or CCSD(T) levels changes the relative energies of the two lowest-energy isomers, and yields the cyclic 1,2,3,4-dithiadiazete slightly lower in energy than linear SNNS.



cyclic S_2N_2 (D_{2h}, ^1A_g) *cis*-SNSN (C_s, $^3A''$) *trans*-SNSN (C_s, $^3A''$) $(SN)_2$ (C_{2v}, $^1A_1$) *trans*-SNNS (C_{2h}, ^3A_u) *linear* SNNS ($D_{\infty h}$, $^1\Sigma_g^+$)

Figure 4. Calculated molecular structures of S_2N_2 isomers at the B3LYP/6-311+G(3df) level of theory. Bond lengths [Å], angles [°] (italics), molecular symmetry, and electronic states are indicated.

In summary, the experimental results provide insights into the complex PES of the S_2N_2. Linear SNNS (j) and cyclic 1,2,3,4-dithiadiazete (g, C_{2v}) were calculated to be lower in energy than the familiar alternate SNSN ring (a, D_{2h}), and singlet *trans* NSSN (h) was predicted to be formed preferentially from two SN ($X^2\Pi$) radicals.[9c] However, apart from the known D_{2h} ring structure none of these S_2N_2 isomers have as yet been detected experimentally. Instead two new triplet bent SNSN and a new cyclic $(SN)_2$ species have been established for the first time, and the formation of triplet *trans* SNNS (C_{2h}, ^3A_u) by photolysis of the matrix-isolated SNSN species is suggested. The present study expands the known chemistry of S_2N_2 and contributes to the ongoing work to unravel the hitherto still unsettled mechanism of the solid-state polymerization of cyclic S_2N_2 (a), in which open-shell SNSN isomers have been suggested to be involved.[5]

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[1] a) T. Chivers, R. Laitininen in *Handbook of Chalgogen Chemistry*: *New Perspectives in Sulfur*, *Selenium and Tellurium*, *Vol. 1*, 2ednd ed(Eds.: F. A. Devillanova, W. W. du Mont), RSC, Cambridge, **2013**, pp. 191 – 237; b) J. Moilanen, A. J. Karttunen, H. M. Tuononen, T. Chivers, *J. Chem. Theory Comput.* **2012**, *8*, 4249 – 4258; c) N. P. Gritsan, A. V. Zibarev, *Russ. Chem. Bull.* **2011**, *120*, 2127 – 2136; d) J. M. Rawson, A. Alberola, A. Whalley, *J. Mater. Chem.* **2006**, *16*, 2560 – 2575; e) T. Chivers in *A Guide to Chalcogen-Nitrogen Chemistry*, World Scientific, London, **2005**.

[2] W. Gregory, *J. Pharm.* **1835**, *21*, 312 – 317.

[3] a) R. T. Boere, T. Chivers, T. L. Roemmele, H. M. Tuononen, *Inorg. Chem.* **2009**, *48*, 7294 – 7306; b) E. A. Pritchina, N. P. Gritsan, T. Bally, A. V. Zibarev, *Inorg. Chem.* **2009**, *48*, 4075 – 4082; c) E. A. Pritchina, D. S. Terpilovskaya, Y. P. Tsentalovich, M. S. Platz, N. P. Gritsan, *Inorg. Chem.* **2012**, *51*, 4747 – 4755.

[4] M. Goehring, D. Voigt, *Naturwissenschaften* **1953**, *40*, 482.

[5] a) A. J. Banister, J. B. Correl, *Adv. Mater.* **1998**, *10*, 1415 – 1429; b) M. M. Labes, P. Love, L. F. Nichols, *Chem. Rev.* **1979**, *79*, 1 – 15.

[6] See, for examples: a) A. Perrin, A. F. Antognini, X. Q. Zeng, H. Beckers, H. Willner, G. Rauhut, *Chem. Eur. J.* **2014**, *20*, 10323 – 10331; b) R. D. Harcourt, *ChemPhysChem* **2013**, *14*, 2859 – 2864; c) T. T. Takaluoma, K. Laasonen, R. S. Laitinen, *Inorg. Chem.* **2013**, *52*, 4648 – 4657; d) R. Evans, A. J. Downs, R. Köppe, S. C. Peake, *J. Phys. Chem. A* **2011**, *115*, 5127 – 5137; e) S. M. Bleay, P. F. Kelly, R. S. P. King, *J. Mater. Chem.* **2010**, *20*, 10100 – 10102; f) T. L. Roemmele, J. Konu, R. T. Boeré, T. Chivers, *Inorg. Chem.* **2009**, *48*, 9454 – 9462.

[7] a) A. L. L. East, *J. Chem. Phys.* **1998**, *109*, 2185 – 2193; b) M. Tobita, S. A. Perera, M. Musial, R. J. Bartlett, M. Nooijen, J. S. Lee, *J. Chem. Phys.* **2003**, *119*, 10713 – 10723.

[8] a) J. R. Warn, D. Chapman, *Spectrochim. Acta* **1966**, *22*, 1371 – 1379; b) C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito, A. J. Heeger, *J. Am. Chem. Soc.* **1975**, *97*, 6358 – 6363.

[9] a) G.-H. Zhang, Y.-F. Zhao, J. I. Wu, P. v. R. Schleyer, *Inorg. Chem.* **2012**, *51*, 13321 – 13327; b) Y. Zhang, Y. Xu, Q. S. Li, *Mol. Phys.* **2007**, *105*, 1883 – 1889; c) R. C. Mawhinney, J. D. Goddard, *Inorg. Chem.* **2003**, *42*, 6323 – 6337.

[10] a) H. Bürger, W. Schneider, S. Sommer, W. Thiel, H. Willner, *J. Chem. Phys.* **1991**, *95*, 5660 – 5669; b) J. Breidung, H. Bürger, C. Kotting, R. Kopitzky, W. Sander, M. Senzlober, W. Thiel, H. Willner, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1983 – 1985; *Angew. Chem.* **1997**, *109*, 2072 – 2075; c) C. S. Jamieson, A. M. Mebel, R. I. Kaiser, *ChemPhysChem* **2006**, *7*, 2508 – 2513; d) F. Kraus, T. Hanauer, N. Korber, *Inorg. Chem.* **2006**, *45*, 1117 – 1123.

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

[12] a) A. J. Bridgeman, B. Cunningham, *Spectrochim. Acta Part A* **2004**, *60*, 471 – 480; b) H. M. Tuononen, R. Suontamo, J. Valkonen, R. S. Laitinen, T. Chivers, *J. Phys. Chem. A* **2005**, *109*, 6309 – 6317.

[13] P. Kambouris, T.-K. Ha, C. Wentrup, *J. Phys. Chem.* **1992**, *96*, 2065 – 2068.

[14] D. S. Warren, M. Zhao, B. M. Gimarc, *J. Am. Chem. Soc.* **1995**, *117*, 10345 – 10352.