Unexpected formation of a sterically protected nitrogen pentasulfide $ArNS_5$ (Ar = 2,6-dimesityl-4-methylphenyl) and the X-ray crystallographic analysis

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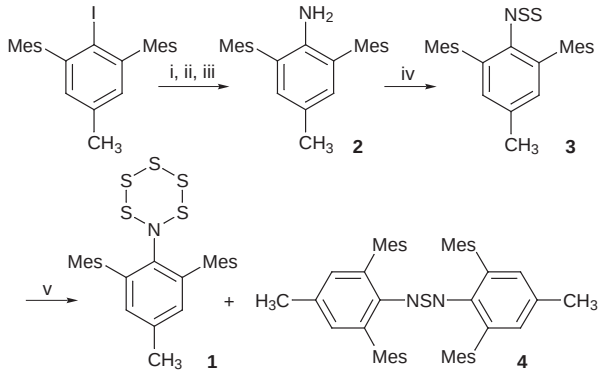
A stable cyclic nitrogen pentasulfide $ArNS_5$ (Ar = 2,6-dimesityl-4-methylphenyl) was unexpectedly obtained by passing the corresponding *N*-thiosulfinylaniline through a silica gel column and the chair form of the six-membered ring was revealed by X-ray crystallographic analysis.

Cyclic nitrogen polysulfides NS_x other than the eight-membered ring were not known for many years due to the lack of an appropriate method of preparation and their instability. Recently, Steudel *et al*. discovered a route to NS_x heterocycles (x = 5, 6, 8, 9, 11)[1] by using titanocene complexes, but most of them turned out to be unstable materials. On the other hand, introduction of sterically demanding groups has played an important role in the isolation of several cyclic polysulfides such as CS_x,[2] but such an attempt at kinetic stabilization of cyclic nitrogen polysulfides has not been reported. Recently, we[3] and Protasiewicz[4] have reported the synthesis of group15 element compounds such as diphosphenes and phosphaarsene possessing sterically protecting groups of the 2,6-diarylphenyl type, which have been successfully used by Power *et al.* for the stabilization of a wide range of compounds from low valent transition metals to main-group element compounds.[5] One of the noteworthy points of the 2,6-dimesityl-4-methylphenyl group is the difference of reactivity of the *ortho* substituents as compared with the widely used 2,4,6-tri-*tert*-butylphenyl group, in spite of the comparable sterically protecting effect.[3] During our systematic study on group 15 compounds possessing the 2,6-dimesityl-4-methylphenyl group, we became interested in *N*-thiosulfinylaniline **3**, since the 2,4,6-tri-*tert*-butylphenyl derivative cyclizes to form a five membered heterocycle despite the bulkiness of the *tert*-butyl group.[6] However, **3** was not so stable as expected and we obtained the stable cyclic nitrogen pentasulfide $ArNS_5$ **1** unexpectedly (Scheme 1).

2,6-Dimesityl-4-methylaniline (**2**) was prepared by $LiAlH_4$ reduction of the corresponding phenyl azide in 96%, which was synthesized from the corresponding iodobenzene by lithiation followed by quenching with *p*-toluenesulfonyl azide in 95%. Oxidation of **2** with MCPBA afforded the corresponding nitrosobenzene‡ as a stable pale green solid in 72% yield similarly to other sterically protected anilines.[7] Sulfurization of **2**† with S_2Cl_2 in the presence of triethylamine[6,8] gave a reddish purple oil, which was assigned as *N*-thiosulfinylaniline **3**. Almost quantitative formation of **3** was confirmed by ^1H NMR. However, **3** decomposed during attempted purification by column chromatography (SiO_2–*n*-hexane) and cyclic nitrogen pentasulfide **1** was isolated in 21% as a yellow solid. *N*,*N*′-Bis(2,6-dimesityl-4-methylphenyl)sulfurdiimide **4** (10%) was another identified product and 61% of aniline **2** was recovered. Pale yellow prisms suitable for X-ray crystallographic analysis were obtained after recrystallization from *n*-hexane.§



Scheme 1 *Reagents and conditions*: i, *n*-BuLi, THF; ii, TsN_3; iii, $LiAlH_4$, diethyl ether; iv, S_2Cl_2, Et_3N, diethyl ether; v, SiO_2

Fig. 1 shows the molecular structure of **1**. The NS_5 ring takes a chair form like CS_5,[9] S_6,[10] and TiS_5[11] heterocycles and the torsion angles within the six-membered ring range from 67.42(5) to 74.88(8)°, which deviate markedly from values of *ca.* 100° of the stable eight-membered rings such as HNS_7[12] and S_8.[13] On the other hand, the bond lengths and angles do not differ greatly from those for HNS_7.[12] The nitrogen atom takes almost planar geometry with the sum of the bond angles around N(1) as 359.57°, and the dihedral angle between the plane

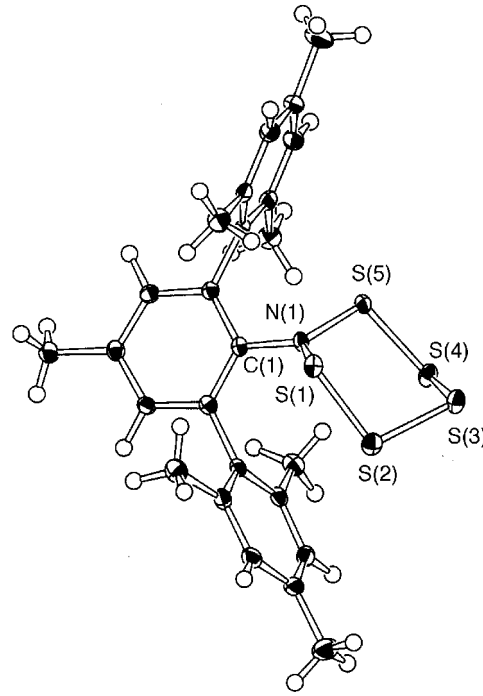


Fig. 1 Molecular structure of **1** in the crystal. ORTEP drawing with 50% probability ellipsoids. Selected bond lengths (Å), bond angles (°), and torsion angles (°): S(1)–N(1) 1.699(1), S(1)–S(2) 2.0612(7), S(2)–S(3) 2.0803(6), S(3)–S(4) 2.0718(6), S(4)–S(5) 2.0704(7), S(5)–N(1) 1.700(1), N(1)–C(1) 1.442(2), S(2)–S(1)–N(1) 104.40(5), S(1)–S(2)–S(3) 100.89(3), S(2)–S(3)–S(4) 99.14(2), S(3)–S(4)–S(5) 102.12(2), S(4)–S(5)–N(1) 104.01(5), S(1)–N(1)–S(5) 116.01(8), S(1)–N(1)–C(1) 121.61(10), S(5)–N(1)–C(1) 121.95(10), S(1)–S(2)–S(3)–S(4) –70.01(3), S(1)–N(1)–S(5)–S(4) 73.29(8), S(2)–S(1)–N(1)–S(5) –74.88(8), S(2)–S(3)–S(4)–S(5) 69.64(3), S(3)–S(2)–S(1)–N(1) 69.20(5), S(3)–S(4)–S(5)–N(1) 69.20(5).

defined by N(1), S(1), S(5), and C(1) and the central benzene ring is 55.07°. The NS_5 ring aligns in the direction of the *b* axis with the short contact less than the sum of van der Waals radii between S(2) and S(5*), S(1) and S(4*) of the neighboring molecules (marked with*), being 3.4102(6) and 3.6219(6) Å, respectively. Although the mechanism of the formation of **1** is not clear at present, oligomerization (stoichiometrically trimerization) of *N*-thiosulfinylaniline **3** followed by elimination of a stable sulfurdiimide **4** might afford **1**, since the electrophilicity of **3** might be enhanced by an acid on the silica gel surface. The ring size could depend on the steric demand or the cavity size made by the two mesityl groups.

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Notes and References

† To a solution of **2** (300 mg, 0.873 mmol) in a mixture of triethylamine (0.3 ml, 2.15 mmol) and diethyl ether (15 ml), a solution of disulfur dichloride (0.09 ml, 1.13 mmol) in diethyl ether (10 ml) was added dropwise at 0 °C to give a red mixture. After being stirred for 1 h at 0 °C, the reaction mixture was poured into ice-water, extracted with diethyl ether, dried over $MgSO_4$, and concentrated to give crude **3** as a red oil almost quantitatively. The oil was submitted to silica-gel column chromatography (gradient elution with *n*-hexane and chloroform) to give **1** (21%) and **4** (10%), together with recovery of **2** (61%). Further recrystallization of **1** from *n*-hexane afforded pure **1** as yellow prisms. **3**: reddish brown oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.05 (2H, s, arom.), 6.87 (4H, s, Mes-arom.), 2.43 (3H, s, CH_3), 2.28 (6H, s, Mes-*p*-CH_3), 2.10 (12H, s, Mes-*o*-CH_3); LRMS (EI, 70 eV) *m/z* 405 (M^+, 8), 341 ($M^+ - 2S$, 62), 326 ($M^+ - 2S - CH_3$, 100), 311 ($M^+ - 2S - 2CH_3$, 25); UV–VIS (CH_2Cl_2) λ_{max} 465 nm. **1**: yellow prisms; mp 133.0–134.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.04 (4H, s, Mes-arom.), 6.84 (2H, s, arom.), 2.37 (6H, s, Mes-*p*-CH_3), 2.34 (3H, s, CH_3), 2.10 (12H, s, Mes-*o*-CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.3, 137.6, 137.5, 137.5, 136.4 , 130.7, 128.7, 21.3, 21.2, 20.9 (one quarternary carbon peak was missing at 295 and 323 K, probably due to dynamic behavior); IR (KBr) 3016, 2947, 2916, 2854, 1612, 1452, 1444, 1423, 1375, 1205, 1182, 1039, 1030, 870, 849, 758 cm^{-1}; UV–VIS (hexanes) $\lambda_{max}(\varepsilon)$ 246.4 (17900) nm ; LRMS (EI, 70 eV) *m/z* 501 (M^+, 0.4), 405 ($M^+ - 3S$, 6), 373 ($M^+ - 4S$, 5), 341 ($M^+ - 5S$, 58), 326 ($M^+ - 5S - CH_3$, 100), 311 ($M^+ - 5S - 2CH_3$, 24), 296 ($M^+ - 5S - 3CH_3$, 11); HRMS (EI, 70 eV) Found: *m/z* 501.0757, calc. for $C_{25}H_{27}NS_5$: *M* 501.0748.

‡ 2,6-Dimesityl-4-methylphenylnitrosobenzene: light green crystals; mp 195.0–196.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.03 (2H, s, arom.), 6.93 (4H, s, Mes-arom.), 2.44 (3H, s, CH_3), 2.34 (6H, s, Mes-*p*-CH_3), 1.87 (12H, s, Mes-*o*-CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 162.6, 146.0 , 136.6, 135.6, 135.5, 133.8, 131.0, 128.7, 21.7, 21.1, 20.6; LRMS (EI, 70 eV) *m/z* 357 (M^+, 100), 340 ($M^+ - CH_3$, 87); UV–VIS (CH_2Cl_2) λ_{max} 810 nm.

§ *Crystal data* for **1**: $C_{25}H_{27}NS_5$, M = 501.79, pale yellow prisms, crystal dimensions 0.60 × 0.50 × 0.40 mm^3, monoclinic, space group *C*2/*c* (no. 15), a = 28.445(7), b = 12.653(2), c = 17.078(2) Å, β = 125.79(1)°, U = 4985(1) $Å^3$, Z = 8, D_c = 1.337 g cm^{-3}, μ = 0.479 mm^{-1}, T = 112(1) K, F(000) = 2112.00. Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-Kα radiation, λ = 0.71070 Å. No. of reflections measured 4405. No. of observations [$I > 3.00\sigma(I)$] 4060. The structure was solved by direct method (SAPI91[14]), expanded using Fourier techniques (DIRDIF94[15]), and refined by full matrix least squares on F for 389 variable parameters. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. R = 0.031 R_w = 0.054 for observed reflections [$I > 3.00\sigma(I)$] and R = 0.034, R_w = 0.058 for all. Goodness of fit S = 1.42. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.26 and −0.29 e $Å^{-3}$, respectively. Structure solution, refinement, and graphical representation were carried out using teXsan package.[16] CCDC 182/994.

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