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NOVEL FORMATION AND MOLECULAR STRUCTURE OF 1,2,3,4,5,6,7,8,9-NONATHIACYCLOUNDEC-10-ENE

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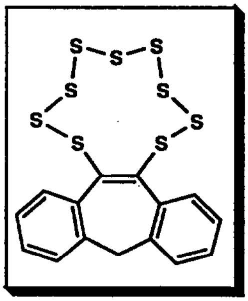
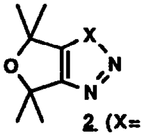
Summary; Thermal reaction of 8,8-dibenzo[3,4;6,7]cyclohepta[1,2-*d*][1,2,3]selenadiazole with elemental sulfur afforded a new type of cyclic polysulfide, 1,2,3,4,5,6,7,8,9-nonathiacycloundec-10-ene (**1**), the novel molecular structure of which was finally determined by X-ray crystallographic analysis.

A considerable interest has focused on the chemistry of cyclic polysulfides from the viewpoints of not only their unique physical and chemical properties but also their biological activities,[3] and recent few years have witnessed a number of reports on the synthesis and reactions of new stable cyclic polysulfides.[4] However, most of them are restricted to 1,2,3-trithiole and 1,2,3,4,5-pentathiepin ring systems, and the cyclopolysulfides containing longer sulfur atom linkage than C_2S_5 ring system are much less common.

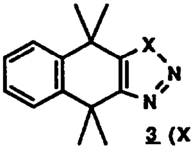
We wish to present here the first synthesis of stable 1,2,3,4,5,6,7,8,9-nonathiacycloundec-10-ene (**1**) together with its crystallographic structure analysis. Recently, we have succeeded in the synthesis of novel cyclic polychalcogenides (**4**, **5**, **6**, **7**, **8**, **9**, and **10**) by the thermal reactions of sterically protected fused 1,2,3-chalcogenadiazoles (**2** and **3**) with elemental sulfur and selenium as shown below.[5] To elucidate the effect of the ring strain and bulkiness of the fused part on the sulfurization of fused 1,2,3-selenadiazole, we have examined the thermal reaction of 8,8-dibenzo[3,4;6,7]cyclohepta[1,2-*d*][1,2,3]selenadiazole (**11**)[6] with elemental sulfur.



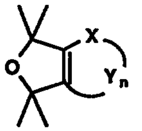
1



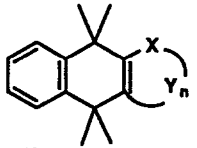
2 (X=S or Se)



3 (X=S or Se)



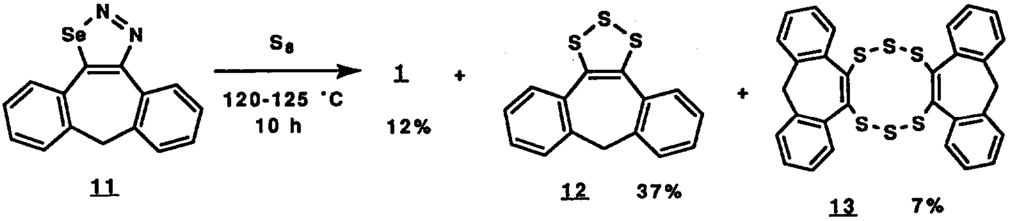
4 (X=Se, Y=S, n=4)
5 (X=Y=S, n=4)
6 (X=Y=S, n=3)
10 (X=Y=Se, n=4)



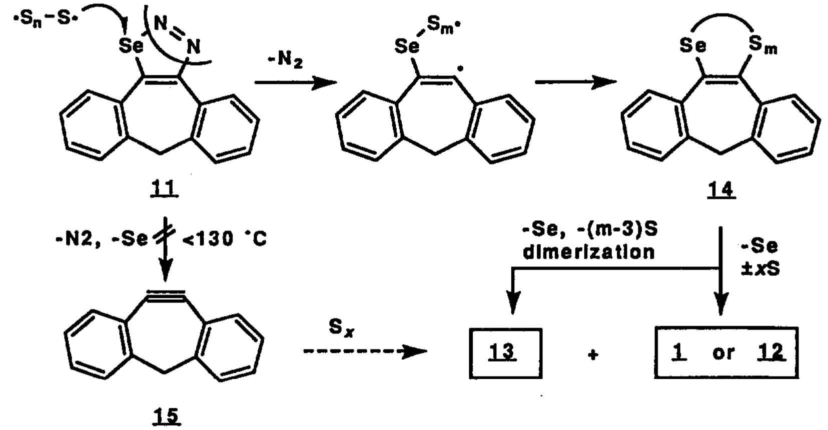
7 (X=Y=S, n=2)
8 (X=Y=S, n=4)
9 (X=Y=Se, n=2)

When the selenadiazole (**11**; 300 mg, 1.01 mmol) was treated with an excess amount of molten sulfur (4.2 g, 16.4 mmol as S_8) at 120-125 °C for 10 h under nitrogen atmosphere, a complicated mixture of sulfurization products was obtained after the separation of excess sulfur. By an exhaustive chromatographic separation (HPLC and TLC) and recrystallization (from hexane), three kinds of cyclopolysulfides, 1,2,3,4,5,6,7,8,9-nonathiacycloundec-10-ene (**1**; 57.9 mg, 12%), 1,2,3-trithiole (**12**; 107.3 mg, 37%), and 1,2,3,6,7,8-

hexathiecin (**13**; 19.1 mg, 7%) were isolated in a stable and colored crystalline form. Although the 1,2,3-trithiole (**12**) and 1,2,3,6,7,8-hexathiecin (**13**) were thermally stable even in refluxing *o*-dichlorobenzene, nonathiacycloundecene (**1**) was fairly labile on heating at 130 °C in *o*-dichlorobenzene to afford an equilibrated mixture of several kinds of polysulfides, the ratio of which was almost the same as that of the crude mixture obtained by the reaction of 1,2,3-selenadiazole (**11**) with elemental sulfur. Similar equilibrated mixture of cyclopolysulfides was also obtained by the reaction of 1,2,3-trithiole (**12**) with excess amount of molten sulfur at 130 °C.

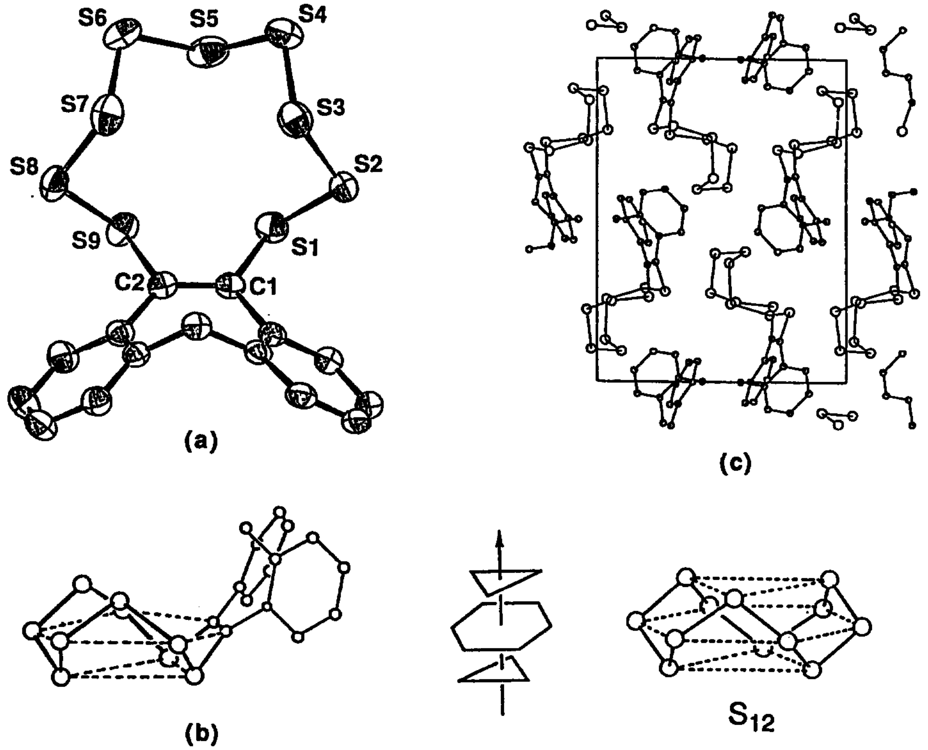


The formation mechanism of these unique cyclopolysulfides from **11** can be rationalized by the initial attack of the activated sulfur radical to the selenium atom of **11** followed by the denitrogenation and cyclization leading to the intermediary cyclopolychalcogenide such as **14**. Since the substrate **11** is inert under the reaction temperature either in solution or in a solid state, the thermal formation of the reactive cyclopentyne intermediate (**15**), which is the alternative key intermediate to form the cyclic polysulfides, is unlikely involved. Meanwhile, we have already reported the relative instability of 1,2,3,4,5-tetrathiaselenepin (**4**) in compared with the corresponding 1,2,3,4,5-pentathiepin (**5**) resulting in a facile formation of 1,2,3,4-tetrathiin (**6**)[5a] and also the thermal equilibraiton between 1,2,3-trithiole (**7**) and 1,2,3,4,5-pentathiepin (**8**).[5c] Therefore, ready thermal dechalcogenation of the intermediate (**14**) and the subsequent ring closure, dimerization, and/or further reaction with excess activated sulfur radical might result in the final formation of the stable cyclopolysulfides **1**, **12**, and **13**. In addition, the successful isolation of these novel cyclopolysulfides without any bulky substituent suggests that the conjugation of the dibenzocycloheptatriene moiety with the polysulfur chain is effective enough to stabilize the cyclopolysulfide ring systems and steric protection is not always essential to the formation and isolation of cyclopolysulfides.



The structures of these newly obtained cyclopolysulfides, **1**, **12**, and **13**, were satisfactorily confirmed by ^{1}H-NMR, ^{13}C-NMR, MS, and UV spectroscopic data together with elemental analysis.[7]

The formation of **1** is of great interest as the first example of cyclopolysulfide with an unprecedentedly long sulfur chain, and the molecular structure of 1 was finally determined by X-ray crystallographic analysis as shown in Figure 1.[8] Of particular note is the remarkable resemblance of the molecular structure, especially in the aspect of sulfur atom stacking, between 1 and cyclododecasulfur (S_{12}),[9] which is the secondly stable allotrope of cyclopolysulfur next to S_8. The bond properties are: S-S bond length = 2.048 ± 0.010 Å, S-S-S bond angle = 106.4 ± 1.7 °, and S-S-S-S torsion angle = 82.7 ± 6.3 °. These values are very similar to those of S_{12}, *i.e.* the unperturbed cyclopolysulfur.[10]



Bond lengths (Å): C1-C2,1.359(4); C1-S1,1.784(3); S1-S2, 2.057(2); S2-S3, 2.048(1); S3-S4, 2.056(1); S4-S5, 2.045(2); S5-S6, 2.308(2); S6-S7, 2.055(2); S7-S8, 2.044(1); S8-S9, 2.054(2); S9-C2, 1.744(3). **Bond angles (°):** C2-C1-S1, 118.1(2); C1-S1-S2, 103.8(1); S1-S2-S3, 105.6(1); S2-S3-S4, 107.7(1); S3-S4-S5, 105.4(1), S4-S5-S6, 106.0(1); S5-S6-S7, 106.2(1); S6-S7-S8, 108.0(1); S7-S8-S9, 104.6(1); S8-S9-C2,103.2(1); S9-C2-C1, 117.4(2).

Figure 1. Molecular drawings of 1 with selected bond lengths and angles; Perspective views ((a) and (b)) and packing of molecules in the unit cell (c).

The similarity of nonathiacycloundecene (1) with S_{12} was also recognized in their vibrational spectra. When the Raman spectra of 1 was taken from powdered sample using the 514.5 nm line of an argon laser in the region 100 to 1700 cm^{-1}, a strong Raman line at 463 cm^{-1} was observed. The frequency value of 1 is almost similar to that of S_{12} (459 cm^{-1})[11] and slightly lower than those of fused 1,2,3,4,5-pentathiepins (485 cm^{-1}).[4b] Further investigation on the reactivity of the novel cyclopolysulfide (1) is now in progress.

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References and Notes

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7. **1**; yellow crystals, mp. 156 °C(decomp.); ^{1}H-NMR(500 MHz, $CDCl_3$) δ 3.857(d, J = 13 Hz, 1H), 3.982(d, J = 13 Hz, 1H), 7.2-7.4(m, 6H), 7.6-7.7(m, 2H); ^{13}C-NMR(125 MHz, $CDCl_3$) δ 40.90(t), 126.49(d), 126.64(d), 129.96(d), 130.30(d), 133.30(s), 142.84(s), 143.65(s); MS, m/z 288(9S, 9%), 286(M-6S, 68%), 256(8S, 22), 254(M-7S, 57), 222(M-8S, 100), 190(M-9S, 7), 163(43), 128(30), 96(24); UV ($CHCl_3$), λ_{max} 328(ε, 9800), 264(22200) nm; IR(KBr) 3064, 2954, 1483, 1439, 758, 613, 470 cm^{-1}; E.A., Found C; 37.71, H; 2.10, S; 59.94%, calcd for $C_{15}H_{10}S_9$ C; 37.62, H; 2.11, S; 60.27%. **12**; red needles, mp. 192 °C(decomp.); ^{1}H-NMR(500 MHz, $CDCl_3$) δ 3.626(d, J = 13 Hz, 1H), 3.778(d, J = 13 Hz, 1H), 7.2-7.4(m, 6H), 7.75-7.85(m, 2H); ^{13}C-NMR(125 MHz, $CDCl_3$) δ 41.37(t), 126.50(d), 127.68(d), 129.66(s), 130.38(d), 131.52(d), 134.78(s), 139.23(s); MS, m/z 286(M$^+$, 51%), 254(M-S, 11), 222(M-2S, 52), 221(100), 190(M-3S, 6), 178(35); Exact mass, m/z obsd 285.9554 calcd for $C_{15}H_{10}S_3$ 285.9935; UV (CH_2Cl_2) λ_{max} 477(ε, 720), 372(430), 305(8600), 255(15600); IR(KBr) 3066, 2924, 2856, 1477, 1437, 762, 615, 458, 420 cm^{-1}. The molecular structure of **12** was also finally determined by X-ray crystallographic analysis, the details of which will be described elsewhere. **13**; yellow crystals, mp. 255 °C(decomp.); ^{1}H-NMR(500 MHz, $CDCl_3$) δ 3.929(d, J = 13 Hz, 1H), 4.661(d, J = 13 Hz, 1H), 7.1-7.4(m, 6H), 7.7-7.8(m, 2H); ^{13}C-NMR(125 MHz, $CDCl_3$) δ 41.18(t), 126.10(d), 126.70(d), 129.77(d), 130.75(d), 133.94(s), 143.13(s), 144.24(s); CIMS, m/z 573(MH$^+$, 2.5%), 541(26), 509(22), 287(80), 255(100), 223 (32); UV(CH_2Cl_2) λ_{max} 368(ε, 4500), 286(28800), 261(30200) nm; IR(KBr) 3060, 2958, 1483, 1439, 756, 613, 474, 420 cm^{-1}; E.A., Found C; 62.52, H; 3.41%, calcd for $C_{30}H_{20}S_6$ C; 62.90, H; 3.51%.
8. Crystal and experimental data for **1**; $C_{15}H_{10}S_9$, MW 478, monoclinic, space group $P2_1/n$, a = 9.508(1), b = 16.298(1), c = 12.468(1) Å, β = 96.77(1) °, V = 1918.6(2) Å^3, D_c = 1.53 g/cm^3, μ(Mo-K_α) 8.98 cm^{-1}, z = 4, R = 0.040 (R_w = 0.049), $W = 1/(A|Fo|^2 + B|Fo| + C)$ and A = 0.0036, B = -0.118, C = 1.337. Data collection was performed by CAD4(Enrauf-Nonius) diffractometer with graphite-monochromated Mo-Kα radiation. The structure was solved by *MULTAN 78* using 3249 reflections, and the program system *UNICS III* was used for calculation. All hydrogen atoms were found in D-fourier method. Refinement: full matrix least squares (Anisotropic thermal parameters for the non-hydrogen atoms, isotropic ones for the hydrogen atoms). Atomic co-ordiantes, bond lengths and angles, and thermal parameters have been deposited at Cambridge X-ray Crystallographic Data Centre. Full details of the crystallographic analysis of **1** will be described in the future as a full paper.

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