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Macrocycles with 1,2-dicyano-1,2-dithioethene units

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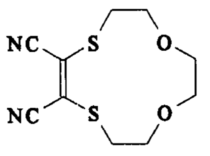
The new unsaturated macrocyclic tetrathioethers (Z,Z)-4 (n = 0), (Z,Z)-5 (n = 1), (Z,Z)-6 (n = 2) and (Z,Z)-7 (n = 3) were synthesized by the cyclization of (Z)-disodium-1,2-dicyanoethene-1,2-dithiolate (Z)-3 with ω,ω'-dibromoalkanes $BrCH_2CH_2(CH_2)_nCH_2Br$ (n = 0;1;2;3) on refluxing in dioxane in yields up to 15%. By reaction of the dithiolate (Z)-3 with 1,3-dibromopropane the unsaturated hexathioether (Z,Z,Z)-6 was also obtained. By the cyclization of dithiolate (Z)-3 with 1,5-dibromopentane and 1,6-dibromohexane the (Z,E)- and (E,E)-isomers, respectively, were formed in addition to the (Z,Z)-isomers. The (E,E)- and (Z,E)-isomers are photochemically convertable to the corresponding themodynamically more stable (Z,Z)-isomers by irradiation with UV-light. The (E,E)-isomers can be synthesized in a straightforward manner using the (E)-disodium-1,2-dicyanoethene-1,2-dithiolate (E)-3. Crystal structures of (Z,Z)-5, (Z,Z)-6, (E,E)-6, (Z,E)-7 and (E,E)-7 are reported.

INTRODUCTION

Aliphatic unsaturated dithioethers are normally poor chelating agents.[1,2] The chelate effect is increased if the 1,2-dithioethene unit is part of a macrocycle.[3] The O_2S_2-coronand **1** with a 1,2-dicyano-1,2-dithioethene unit is a selective ligand for $PdCl_2$.[3] Complexes in which a late transition metal ion is coordinated by two 1,2-dithioethene units of a macrocycle are rare. Schrauzer et al. have synthesized the $NiBr_2$-complex of the macrocyclic tetrathioether **2** which incorporates two 1,2-diphenyl-1,2-dithioethene units.[4]

We are interested in the complexing abilities of macrocycles with two 1,2-dicyano-1,2-dithioethene units for d^8-late transition metal ions. Therefore, we have synthesized a homologous series of macrocyclic unsaturated tetrathioethers containing two 1,2-dicyano-1,2-dithioethene units connected by noncoordinating and flexible polymethylene bridges. The investigation of the metal complexing ability of these novel macrocyclic unsaturated tetrathioethers is the subject of a forthcoming report.



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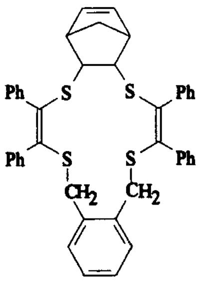

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SYNTHESES

The new unsaturated macrocyclic tetrathioethers with two 1,2-dicyano-1,2-dithioethene units **(Z,Z)-4** (n = 0), **(Z,Z)-5** (n = 1), **(Z,Z)-6** (n = 2) and **(Z,Z)-7** (n = 3) were synthesized by cyclization of (Z)-disodium-1,2-dicyanoethene-1,2-dithiolate **(Z)-3** with ω,ω'-dibromoalkanes $BrCH_2CH_2(CH_2)_nCH_2Br$ (n = 0;1;2;3) under high dilution conditions on refluxing in dioxane in yields up to 15% (Scheme 1).

By the reaction of the dithiolate **(Z)-3** with 1,3-dibromopropane (n = 0), the trimer **(Z,Z,Z)-4** was formed in addition to the dimer **(Z,Z)-4** and the monomer **(Z)-4**. The macrocycle **(Z,Z,Z)-4** is the first example of an unsaturated macrocyclic hexathioether with three 1,2-dithioethene units. A trimeric cyclization product was only found for n = 0. By cyclization of the dithiolate **(Z)-3** with 1,4-dibromobutane (n = 1) the monomer **(Z)-5** was detected in addition to the dimer **(Z,Z)-5**. For the reaction with 1,5-dibromopentane (n = 2) and

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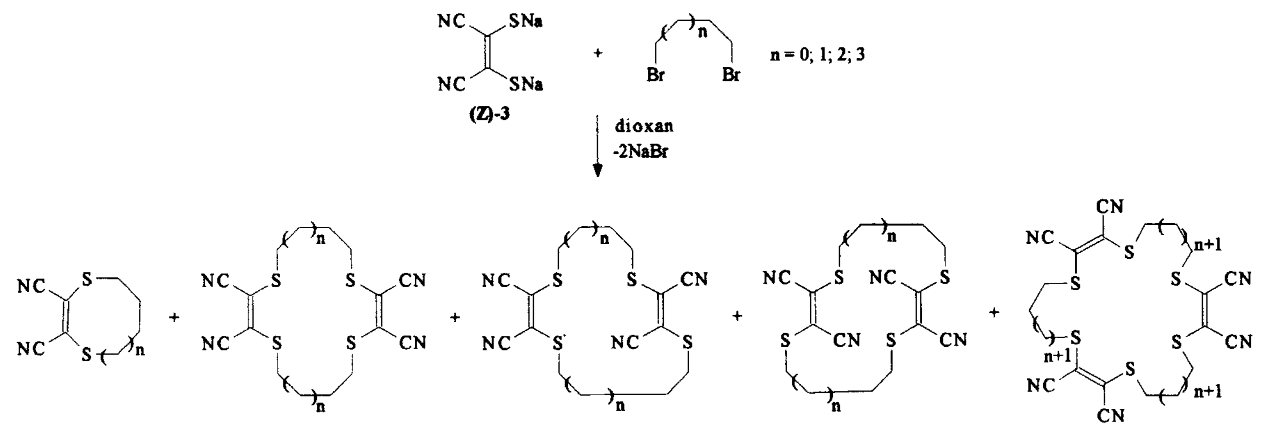


n	monomers	dimers			trimer
0	**(Z)-4** 10%	**(Z,Z)-4** 10%	-	-	**(Z,Z,Z)-4** 1%
1	**(Z)-5** 2%	**(Z,Z)-5** 15%	-	-	-
2	-	**(Z,Z)-6** 8%	**(Z,E)-6** 10%	**(E,E)-6** 2%	-
3	-	**(Z,Z)-7** 6%	**(Z,E)-7** 7%	**(E,E)-7** 2%	-

Scheme 1 Cyclization products of the reaction of (Z)-disodium-1,2-dicyanoethene-1,2-dithiolate **(Z)-3** with ω,ω'-dibromoalkanes $BrCH_2CH_2(CH_2)_nCH_2Br$ (n = 0;1;2;3) on refluxing in dioxan

1,6-dibromohexane (n = 3) the formation of monomers was not observed because the probability of the formation of nine- and ten-membered rings is relatively low.

In the case of n = 2 and n = 3, the (Z,E)- and (E,E)-isomers were also isolated. The formation of (Z,E)- and (E,E)-isomers could be explained by thermally initiated Z→E-isomerization of intermediate products. The structures of the different geometrical isomers were followed from the intensity of the ν(C = C)-band, the position of the wavelength of the maximum absorption (λ_{max}) (Table 1) and photochemical E→Z-isomerizations. The IR-spectra show a strong ν(C = C) band for the (Z,Z)-isomers **(Z,Z)-6** and **(Z,Z)-7**, a medium one for the (Z,E)-isomers **(Z,E)-6** and **(Z,E)-7** and a very weak one for the (E,E)-isomers **(E,E)-6** and **(E,E)-7**. As already observed in the UV-spectra of the two isomers bis(methylthio)fumaronitrile **(E)-8** and bis-(methylthio)maleonitrile **(Z)-8**, the (E,E)-isomers absorb at longer wavelength with lower intensity than the corresponding (Z,Z)-isomers.[5] The longest wavelength absorption band of **(E,E)-6** and **(E,E)-7** is shifted bathochromically by 17 and 33 nm, respectively, compared to λ_{max} of **(Z,Z)-6** and **(Z,Z)-7**.

Table 1 m.p. [°C], R_f-values (CH_2Cl_2), position and intensity of the ν(C=C)-band [cm^{-1}] and of the λ_{max} [nm] (lgε) for **(Z,Z)-4**, **(Z,Z,Z)-4**, **(Z,Z)-5**, **(Z,Z)-6**, **(Z,E)-6**, **(E,E)-6**, **(Z,Z)-7**, **(Z,E)-7**, **(E,E)-7**, **(Z)-8** and **(E)-8**

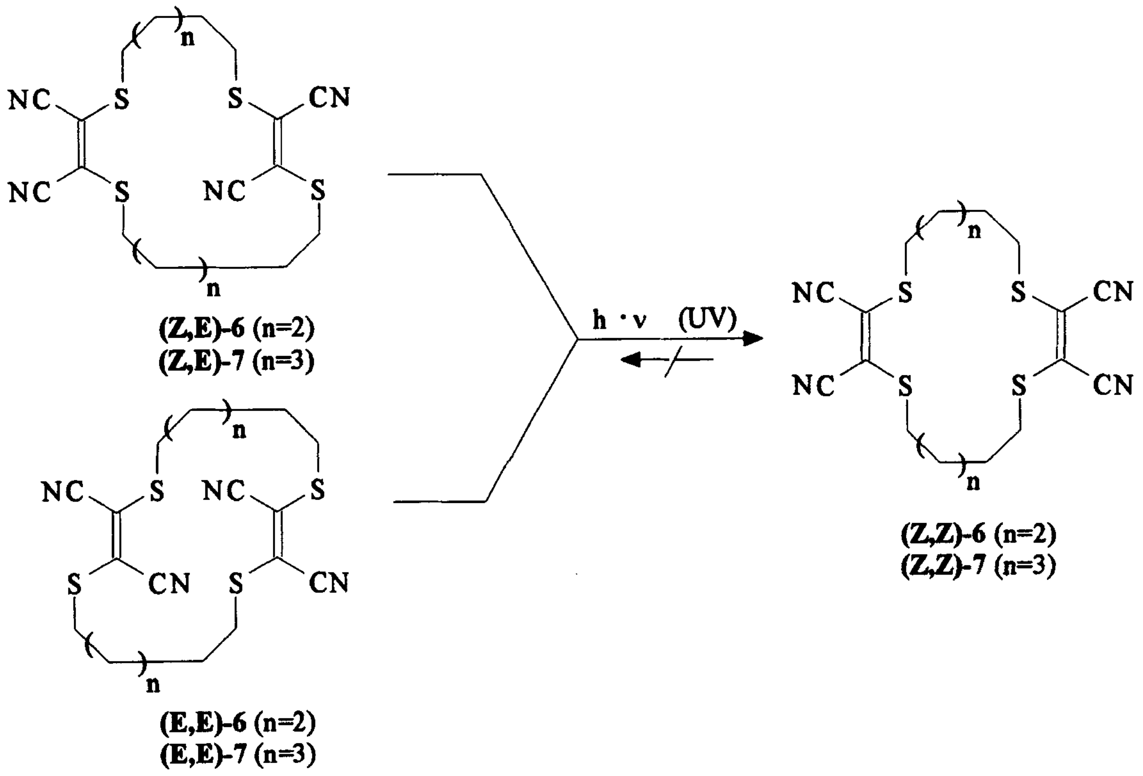
	IR (KBr): ν(C=C) [cm^{-1}]	UV ($CHCl_3$): λ_{max} [nm] (lgε)
(Z,Z)-4	1501 s	338 (4.28)
(Z,Z,Z)-4	1504 s	331 (4.54)
(Z,Z)-5	1500 s	327 (4.47)
(Z,Z)-6	1499 s	341 (4.45)
(Z,E)-6	1504 m	345 (4.28), 373 (4.08) sh
(E,E)-6	1523 w	358 (4.23)
(Z,Z)-7	1509 s	342 (4.43)
(Z,E)-7	1508 m	343 (4.35), 375 (3.98) sh
(E,E)-7	1500 w	365 (4.30)
(Z)-8	1493 s[1)]	342 (4.17)
(E)-8	-[1)]	370 (4.06)

[1)] ref.[5]

Dichloromethane solution containing (Z,E)- and (E,E) -isomers are isomerized quantitively to the (Z,Z)-isomers under broad spectrum ultraviolett irradiation as shown by Simmons et al. in the case of **(E)-8**.[5] Photoisomerization of the (Z,Z)- to the (Z,E)- or (E,E)-isomers is not possible (Scheme 2). This observation should be similar to the case of the isomers **(Z)-8** and **(E)-8**, where the (Z)-isomer is thermodynamically more stable than the (E)-isomer.[5]

By the cyclization of the dithiolate **(Z)-3** with 1,4-dibromobutane the isomers **(Z,E)-5** and/or **(E,E)-5** were formed in addition to **(Z)-5** and **(Z,Z)-5**. This was concluded from the formation of an isosbestic point in the UV-spectrum of the sixteen-membered cyclization products by irradiation with UV-light. The same R_f-values of the different isomers in various solvents prevent a work-up via column chromatography. Pure **(Z,Z)-5** was obtained by irradiation of a dichloromethane solution containing the mixture of isomers with UV-light for one hour.

The (E,E)-isomers can be synthesized in a straightforward manner by using the (E)-disodium-1,2-dicyanoethene-1,2-dithiolate **(E)-3**. **(E,E)-7** was obtained by cyclization of **(E)-3** with 1,6-dibromohexane (Scheme 3) and isolated by fractional crystallization in yields of 8%.



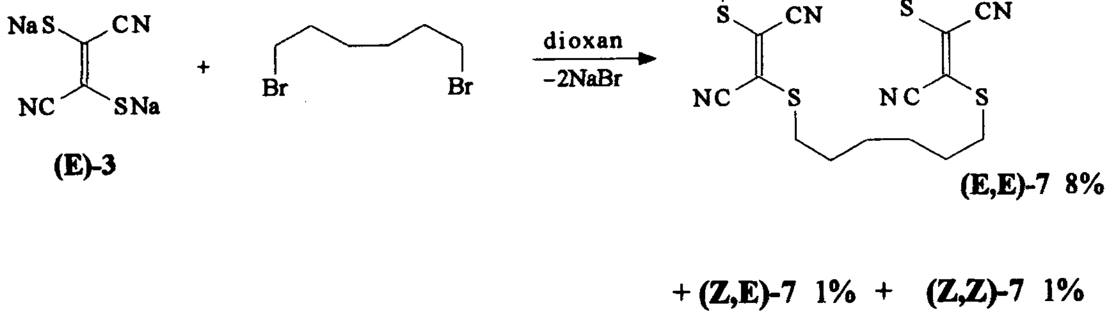
Scheme 2 E→Z-photoisomerization of (Z,E)- and (E,E)-isomers, resp., to the (Z,Z)-isomers in CH_2Cl_2 by irradiation with UV-light ($c_{macrocycle} = 10^{-3}$ mol/l)

CRYSTAL STRUCTURES

The structures of the macrocycles **(Z,Z)-5**, **(Z,Z)-6**, **(E,E)-6**, **(Z,E)-7** and **(E,E)-7** are depicted in Figures 1-5. Bond distances and angles are comparable with those of other macrocycles containing a (Z)-1,2-dicyano-1,2-dithioethene[6] or a (E)-1,2-dicyano-1,2-dithioethene unit.[7] The data for **(Z,Z)-5** and **(E,E)-6** are given in Tables 2 and 3, respectively. Torsion angles for **(Z,Z)-5**, **(Z,Z)-6**, **(E,E)-6**, **(Z,E)-7** and **(E,E)-7** can be found in Tables 4-7. In the crystalline state **(Z,Z)-5** adopt a "chair"-like conformation (Fig. 1) and **(Z,Z)-6** a "boat"-like (Fig. 2) conformation. In these macrocycles the rigid and bulky (Z)-1,2-dicyano-1,2-dithioethene fragments are responsible for a restricted exodentate orientation of the sulfur atoms. This should be useful for chelation of a late transition metal ion in the hole of the macrocycles.

(Z,Z)-5 crystallizes in the centrosymmetric space group C2/m. The more flexible macrocycle 1,6,11,16-tetrathiocycloicosane[8], has four -$S(CH_2)_4S$-sides. Two sides exhibit the same sequence g^- a g^+ as we observe for C3-C3' and C3''-C3''' (Fig. 1, Table 4). For every molecule of **(Z,Z)-5** one molecule of benzene is in the crystal lattice (Fig. 1). The molecular planes of **(Z,Z)-5** and benzene bisect each other at an angle of 90°.

In **(Z,Z)-6** the pentamethylene sides are generated by



Scheme 3 Synthesis of (E,E)-7

Table 2 Selected bond distances [pm] and angles [deg.] for **(Z,Z)-5**.

S1-C3	180.35(7)	C3-S1-C2	102.25(3)
S1-C2	173.77(7)	S1-C3-C4	113.20(3)
C4-C3	151.64(6)	C3-C4-C4'	112.83(3)
C2-C2'''	136.28(5)	S1-C2-C2'''	121.14(3)
C4-C4'	150.48(6)	S1-C2-C21	119.87(3)
C2-C21	142.85(5)	C2-C21-N21	178.12(3)
C21-N21	114.08(4)	C21-C2-C2'''	118.86(3)

g^+ g^+ a g^+ sequence of -C-C-torsion angles (Table 5, Fig. 2). In the isomeric **(E,E)-6** these sides exhibit an a a a a sequence (Table 5). The crystal lattice of **(E,E)-6** contains one disordered molecule dichloromethane per molecule of (E,E)-6. The two (E)-1,2-dicyano-1,2-dithioethene units in **(E,E)-6** are almost in a "syn-like"-arrangement (Fig. 3).

With a longer polymethylene bridge, packing effects are more important for the conformations of the macrocycles. The hexamethylene sequences in **(Z,E)-7** and **(E,E)-7** enable the macrocycles to form relatively unstrained conformations. In **(Z,E)-7** the hexamethylene sides (C5–C10 and C15–C20) are generated by g^+ a a a g^+ and a a g^+ a g^+ sequences of -C-C- torsion angles, respectively. (Table 6, Fig. 4). Both hexamethylene sides of **(E,E)-7** exhibit a g^+ a a a g^+ sequence of -C-C-torsion angles (Table 7).

In **(E,E)-7** repulsive forces between the cyanogroups of the (E)-1,2-dicyano-1,2-dithioethene units and packing effects generate an almost quadrangular cavity of 318.9(5) pm (Fig. 5), which could be useful for the complexation of electron rich linear guests. In **(E,E)-7** the two (E)-1,2-dicyano-1,2-dithioethene units arranged in an "anti-like" form.

Table 3 Selected bond distances [pm] and angles [deg.] for **(E,E)-6**.

S1-C2	175.8(4)	S1-C2-C3	122.5(4)
C2-C3	135.6(5)	C2-C3-S4	122.9(3)
C3-S4	174.9(3)	C3-S4-C5	101.2(2)
S4-C5	182.6(4)	S4-C5-C6	111.0(3)
C5-C6	150.8(7)	C5-C6-C7	113.8(4)
C6-C7	153.5(5)	C6-C7-C8	109.9(3)
C7-C8	151.7(6)	C7-C8-C9	112.8(3)
C8-C9	151.6(5)	C8-C9-S10	111.9(3)
C9-S10	182.6(5)	C9-S10-C11	99.7(2)
S10-C11	176.3(3)	S10-C11-C12	122.9(3)
C11-C12	134.1(5)	C11-C12-S13	123.1(3)
C12-S13	175.2(3)	C12-S13-C14	101.3(2)
S13-C14	181.4(3)	S13-C14-C15	111.6(3)
C14-C15	152.5(5)	C14-C15-C16	113.6(3)
C15-C16	151.7(5)	C15-C16-C17	109.3(3)
C16-C17	153.1(5)	C16-C17-C18	112.7(3)
C17-C18	151.6(5)	C17-C18-S1	112.0(3)
C18-S1	182.8(4)	C18-S1-C2	99.4(2)
C2-C21	144.1(8)	C2-C21-N21	175.8(5)
C3-C31	144.3(6)	C3-C31-N31	176.1(4)
C11-C111	143.9(7)	C11-C111-N111	174.4(5)
C12-C121	143.4(6)	C12-C121-N121	174.2(4)
C21-N21	114.(1)	S1-C2-C21	117.0(3)
C31-N31	111.9(8)	S4-C3-C31	117.8(3)
C111-N111	114.(1)	S10-C11-C111	116.5(3)
C121-N121	116.2(7)	S13-C12-C121	117.6(3)

In all macrocycles the 1,2-dicyano-1,2-dithioethene units are not exactly planar. The two halves NC-C-S are twisted by an angle of 6–12°. This was already observed in the case of bis(methylthio)maleonitrile.[9]

EXPERIMENTAL

General

Solvents were dried and distilled before use. (Z)-disodium-1,2-dicyanoethene-1,2-dithiolate **(Z)-3** was prepared by dimerization of sodium cyandithioformiate. Sodium cyandithioformiate was synthesized by reaction of sodium cyanide with carbon disulfide in dimethylformamide solution.[10] Spectra were recorded on the following instruments: IR: Nicolet 205 FT-IR Spectrometer, UV: UV-VIS-SPECORD M40, NMR: Bruker 250, MS: Finnigan MAT.

X-Ray structure determinations

Single crystals of the macrocycle **(Z,Z)-5** are available from the solvent mixture benzene/hexane. The single crystals of the compounds **(Z,Z)-6**, **(E,E)-6**, **(Z,E)-7** and **(E,E)-7** were grown from dichloromethane/hexane solution. The crystall lattice of **(E,E)-6** contains per molecule one disordered molecule dichloromethane. Therefore, a low-temperature-measurement was necessary. The X-ray data were collected on a Hilger & Watts (Y290) diffractometer for **(Z,Z)-5** on a CAD4 diffractometer for **(Z,Z)-6**, **(E,E)-6**, **(Z,E)-7** and on a P4 diffractometer for **(E,E)-7**. The structures were solved by direct methods and refined with SCHELXL-93.[11–13]

The crystal data for **(Z,Z)-5**: $[C_{16}H_{16}N_4S_4 \cdot C_6H_6]$, $M_r = 392.59 + 78.11$, monoclinic, C2/m, a = 1063.9(2), b = 1426.4(3), c = 821.5(2) pm, $\beta = 103.42(3)°$, $V = 1212.6(5) \cdot 10^6$ pm^3, $D_x = 1.289$ g·cm^{-3}, Z = 2, λ(Mo-Kα) = 71.073 pm, $\mu = 4.1$ cm^{-1}, T = 293 K, final R = 0.051.

Crystal data for **(Z,Z)-6**: $[C_{18}H_{20}N_4S_4]$, $M_r = 420.64$, orthorhombic, Pccn, a = 1541.4(2), b = 1644.0(2), c = 1707.0(2) pm, $V = 4325.6(9) \cdot 10^6$ pm^3, $D_x = 1.292$ g·cm^{-3}, Z = 8, λ(Cu-Kα) = 154.178 pm, $\mu = 41.1$ cm^{-1}, T = 293 K, final R = 0.058.

Crystal data for **(E,E)-6**: $[C_{18}H_{20}N_4S_4 \cdot CH_2Cl_2]$, $M_r = 420.64 + 84.93$, triclinic, P−1, a = 1116.0(1), b = 1118.5(1), c = 1211.6(2) pm, $\alpha = 84.51(1)$, $\beta = 65.63(1)$, $\gamma = 61.94(1)°$, $V = 1206.5(3) \cdot 10^6$ pm^3, $D_x = 1.392$ g·cm^{-3}, Z = 2, λ(Cu-Kα) = 154.178 pm, $\mu = 57.6$ cm^{-1}, T = 173 K, final R = 0.074.

Crystal data for **(Z,E)-7**: $[C_{20}H_{24}N_4S_4]$, $M_r = 448.70$, triclinic, P−1, a = 1004.2(1), b = 1107.6(1), c = 1191.9(1) pm, $\alpha = 65.58(1)$, $\beta = 80.46(1)$, $\gamma = 69.99(1)°$, $V = 1133.8(3) \cdot 10^6$ pm^3, $D_x = 1.314$ g·cm^{-3}, Z = 2, λ(Cu-Kα) = 154.178 pm, $\mu = 39.5$ cm^{-1}, T = 173 K, final R = 0.065.

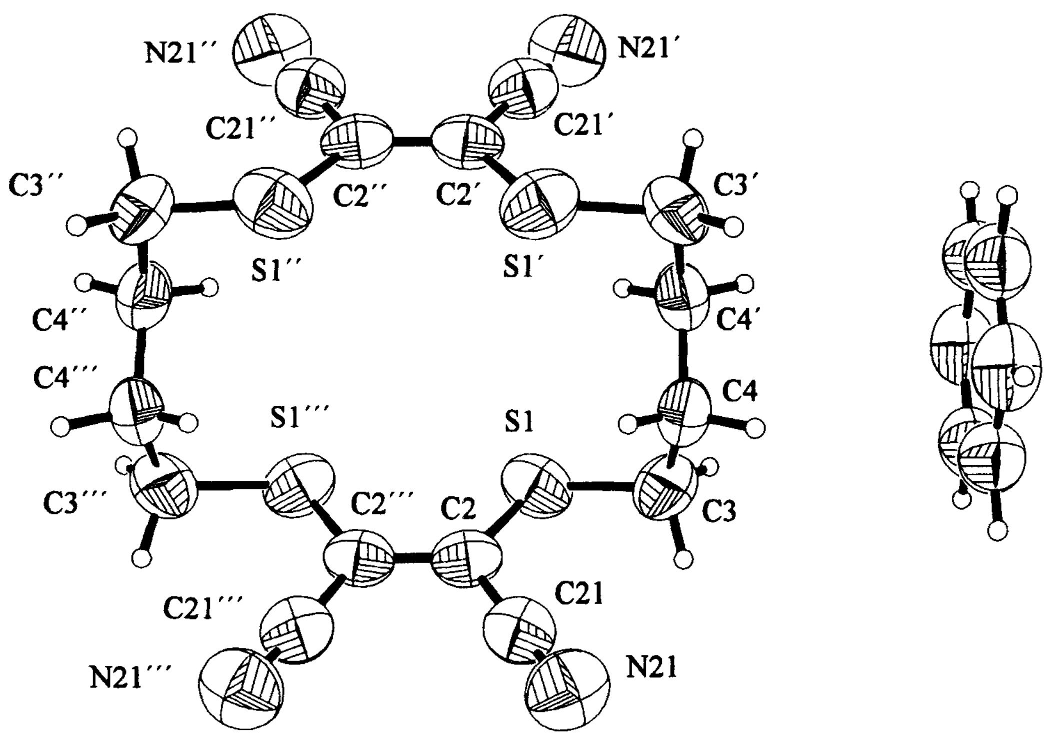


Figure 1 ORTEP illustration of **(Z,Z)-5**

Crystal data for **(E,E)-7**: $[C_{20}H_{24}N_4S_4]$, M_r = 448.70, monoclinic, C2/c, a = 2152.7(3), b = 1091.4(2), c = 1044.9(2) pm, β = 105.52(1)°, V = 2365.4(7)·10^6 pm^3, D_x = 1.260 g·cm^{-3}, Z = 8, λ(Cu-Kα) = 154.178 pm, μ = 37.9 cm^{-1}, T = 173 K, final R = 0.13.

Cyclization of (Z)-disodium-1,2-dicyanoethene-1,2-dithiolate ***(Z)-3*** *with ω,ω'-dibromoalkanes $BrCH_2CH_2(CH_2)_nCH_2Br$ (n = 0;1;2;3):*

5.58 (30mmol) (Z)-disodium-1,2-dicyanoethene-1,2-dithiolate **(Z)-3** was added to a solution of 30 mmol ω,ω'-dibromoalkane (6.06 g 1,3-dibromopropane, 6.48 g 1,4-dibromobutan, 6.90 g 1,5-dibromopentan, 7.32 1,6-dibromohexane) in 670 mL dioxane under an argon atmosphere, protected from light. The reaction suspension was refluxed with stirring for 72 h. Sodium chloride and polymeric reaction products were filtrated off. The filtrate was evaporated to dryness, the residue was taken up in chloroform, washed twice with a saturated solution of sodium chloride and dried over magnesium sulfate. The drying agent was removed by filtration, the filtrate was concentrated in vacuo. The residual brown oil was separated by column chromatography on silica gel 60 with dichloromethane. After evaporation of dichloromethane the products were recrystallized from dichloromethane/hexane.

Cyclization of **(Z)-3** with 1,3-dibromopropane: (Z,Z)-1,4,8,11-Tetrathiacyclotetradec-2,9-diene-2,3,9,10-tetracarbonitrile **(Z,Z)-4**: yield: 0.09 g (5%), pale yellow prisms; m.p.: 236–238°C; R_f: 0.45 (dichloromethane); MS (12eV, 290°C): m/z(%) = 364 (100) [M^+]; IR (KBr): = 2223 cm^{-1} m, 2201 s (C ≡ N); 1501 s (C = C); UV (chloroform): $\lambda_{max}(lg\epsilon)$ = 286 nm (3.98) sh, 338 (4.28); ^1H-NMR ($CDCl_3$): δ = 1.97 ppm (p, 1H, CH_2), 2.10 (m, 3H, CH_2), 2.83 (m, 1H, SCH_2), 3.21 (m, 6H, SCH_2), 3.38 (m, 1H, SCH_2); ^{13}C-NMR (CD_2Cl_2): δ = 28.4 ppm, 31.1, 32.8, 34.2 (1:0.45:0.23:0.56) CCH_2); 112.6 (C≡N); 123.2 (C=C); $C_{14}H_{12}N_4S_4$ (364.53); Calcd.: C 46.13 H 3.32 N 15.37 S 35.18; Found: C 45.69 H 3.39 N 15.01 S 35.10 (Z,Z,Z)-1,4,8,11,15,18-

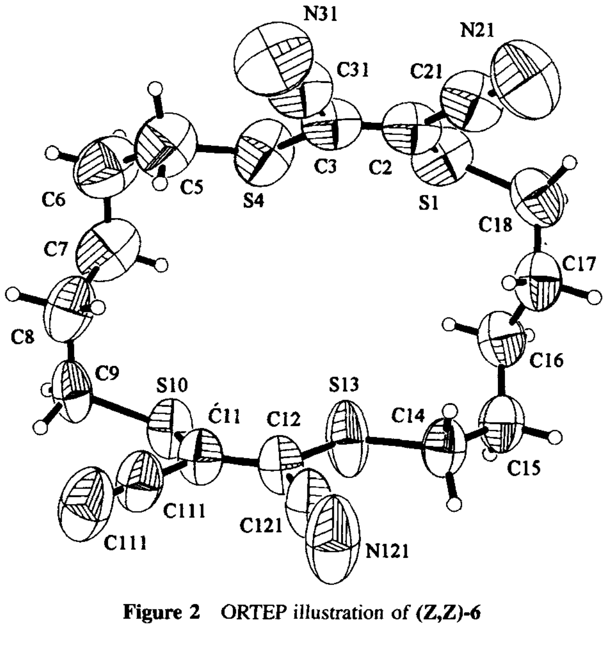


Figure 2 ORTEP illustration of **(Z,Z)-6**

Table 4 Selected torsion angles [deg.] for **(Z,Z)-5**

C4-C3-S1-C2	−74.11(3)	S1'''-C2'''-C2-C21	−175.66(3)
C3-S1-C2-C2'''	166.37(3)	C21-C2-C2'''-C21'''	0.00(3)
S1-C2-C2'''-S1'''	0.02(3)	C3-S1-C2-C21	−18.02(3)
S1-C3-C4-C4'	−72.30(3)	C3-C4-C4'-C3'	167.25(3)

Hexathiacycloheneicos-2,9,16-triene-2,3,9,10,16,17-hexacarbonitrile **(Z,Z,Z)-4**: yield: 0.16 g (1%), white amorphous solid; m.p.: 205°C; R_f: 0.30 (dichloromethane); MS (70eV): m/z(%) = 546 (35) $[M^+]$; IR (KBr): =2218 cm^{-1} m, 2208 s (C≡N), 1504 s (C=C); UV (chloroform): λ_{max}(lgε) = 278 nm (4.07) sh, 331 (4.54), 338 (4.53) sh; ^{1}H-NMR ($CDCl_3$): δ = 2.15 ppm (p, 6H, CH_2), 3.22 (t, 12H, SCH_2); ^{13}C-NMR ($CDCl_3$): δ = 30.5 ppm (CH_2), 33.3 (SCH_2), 111.8 (C≡N), 122.2 (C=C); $C_{21}H_{18}N_6S_6$ (546.80); Calcd.: C 46.13 H 3.32 N 15.37 S 35.18; Found: C 45.99 H 3.26 N 14.19 S 34.85;

Cyclization of **(Z)-3** with 1,4-dibromobutane: Recrystallized sixteen-membered cyclization products were solved in dichloromethane and irradiated with UV-light. After evaporation of the solvent the residue was recrystallized from dichloromethane/hexane. (Z,Z)-1,4,9,12-Tetrathiacyclohexadec-2,10-diene-2,3,10,11-tetracarbonitrile **(Z,Z)-5**: yield: 1.77 g (15%), colorless prisms; m.p.: 243–245°C; R_f: 0.53 (dichloromethane); MS (70eV): m/z(%) = 392 (43) $[M^+]$, 88 (100) $[C_4H_8S]^+$; IR (KBr): =2208 cm^{-1} s (C≡N), 1500 s (C=C); UV (chloroform): λ_{max}(lgε) = 280 nm (4.00), 327 (4.47), 339 (4.42) sh; ^{1}H-NMR ($CDCl_3$): δ = 1.81 ppm (m, 8H, CH_2), 3.16 (m, 6H, SCH_2), 3.24 (t, 2H, SCH_2); ^{13}C-NMR ($CDCl_3$): δ = 28.2 ppm, 28.5 (0.41:1) (CH_2); 33.9, 34.5, 34.7 (0.59:0.80:1) (SCH_2); 111.5, 111.6, 112.0 (0.47:0.54:1) (C≡N); 121.4, 122.2, 122.9 (0.53:1:0.39) (C=C); $C_{16}H_{16}N_4S_4$ (392.59); Calcd.: C 48.95 H 4.11 N 14.27 S 32.67; Found: C 48.86 H 4.08 N 14.19 S 32.32;

Cyclization of **(Z)-3** with 1,5-dibromopentane: (Z,Z)-1,4,10,13-Tetrathiacyclooctadec-2,11-diene-2,3,11,12-tetracarbonitrile **(Z,Z)-6**: yield: 1.01 g (8%), colorless

Table 5 Selected torsion angles [deg.] for **(Z,Z)-6** and **(E,E)-6**

	(Z,Z)-6	(E,E)-6
S1-C2-C3-S4	5.1(5)	167.4(2)
C2-C3-S4-C5	173.0(3)	141.1(3)
C3-S4-C5-C6	−178.2(3)	−68.1(3)
S4-C5-C6-C7	69.0(4)	−179.8(2)
C5-C6-C7-C8	72.1(4)	179.7(3)
C6-C7-C8-C9	178.7(3)	177.8(3)
C7-C8-C9-S10	67.0(4)	−177.2(2)
C8-C9-S10-C11	73.9(3)	69.8(3)
C9-S10-C11-C12	−153.3(3)	−112.3(3)
S10-C11-C12-S13	4.0(5)	−167.3(2)
C11-C12-S13-C14	174.6(4)	−141.8(3)
C12-S13-C14-C15	178.9(4)	67.3(2)
S13-C14-C15-C16	70.6(6)	179.4(2)
C14-C15-C16-C17	71.9(7)	−179.3(2)
C15-C16-C17-C18	179.5(4)	−177.1(2)
C16-C17-C18-S1	64.9(4)	177.2(2)
C17-C18-S1-C2	75.4(3)	−70.0(2)
C18-S1-C2-C3	−158.7(3)	112.8(3)
S1-C2-C3-C31	−170.9(3)	−10.3(5)
S4-C3-C2-C21	179.7(3)	−10.0(5)
S10-C11-C12-C121	−173.3(3)	8.8(5)
S13-C12-C11-C111	179.6(3)	10.8(5)
C21-C2-C3-C31	3.8(6)	172.2(4)
C111-C11-C12-C121	2.2(6)	−173.2(4)
C18-S1-C2-C21	26.7(4)	−69.7(4)
C5-S4-C3-C31	−11.1(4)	−41.1(3)
C9-S10-C11-C111	31.1(4)	69.5(3)
C14-S13-C12-C121	−8.0(4)	42.1(3)

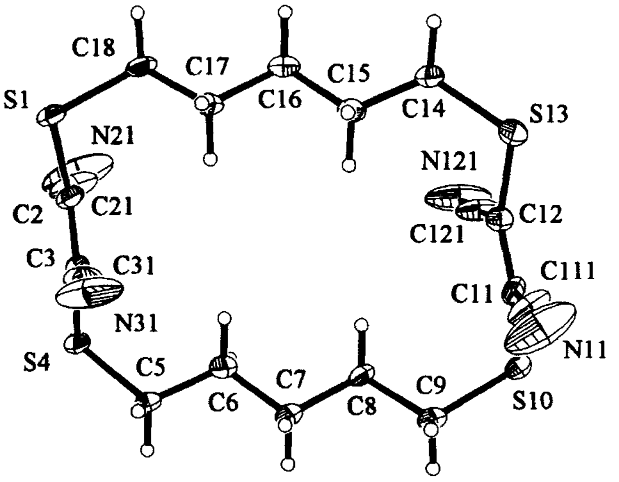


Figure 3 ORTEP illustration of **(E,E)-6**

Table 6 Selected torsion angles [deg.] for **(Z,E)-7**

S1-C2-C3-S4	3.7(3)	S1-C2-C3-C31	−167.9(2)
C2-C3-S4-C5	161.9(2)	S4-C3-C2-C21	179.6(2)
C3-S4-C5-C6	−83.2(2)	S11-C12-C13-C131	4.4(3)
S4-C5-C6-C7	67.7(3)	S14-C13-C12-C121	7.3(3)
C5-C6-C7-C8	170.9(2)		
C5-S4-C3-C31	−26.3(2)	C21-C2-C3-C31	8.0(4)
C6-C7-C8-C9	−167.1(2)	C121-C12-C13-C131	−179.0(2)
C7-C8-C9-C10	176.1(2)		
C8-C9-C10-S11	68.8(3)		
C9-C10-S11-C12	59.9(2)		
C10-S11-C12-C13	−141.2(2)		
S11-C12-C13-S14	−169.3(1)	C20-S1-C2-C21	21.7(2)
C12-C13-S14-C15	−150.1(2)	C5-S4-C3-C31	−26.3(2)
C13-S14-C15-C16	67.1(2)	C10-S11-C12-C121	42.1(2)
S14-C15-C16-C17	175.0(2)	C15-S14-C13-C131	36.1(2)
C15-C16-C17-C18	−177.7(3)		
C16-C17-C18-C19	63.5(4)		
C17-C18-C19-C20	170.1(2)		
C18-C19-C20-S1	59.2(3)		
C19-C20-S1-C2	72.8(2)		
C20-S1-C2-C3	−162.4(2)		

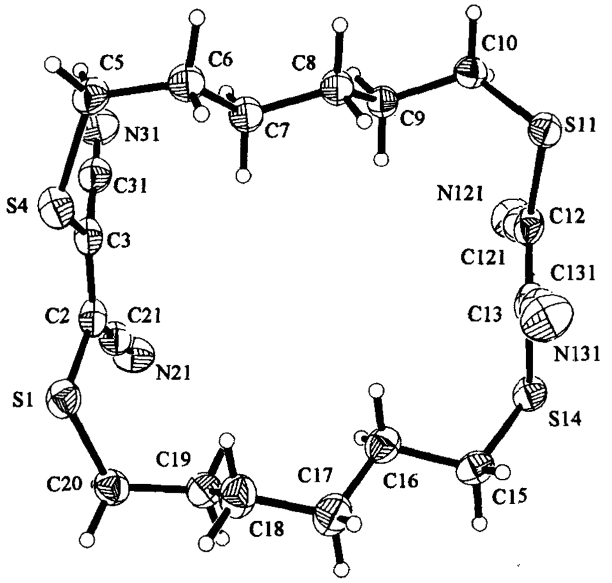


Figure 4 ORTEP illustration of **(Z,E)-7**

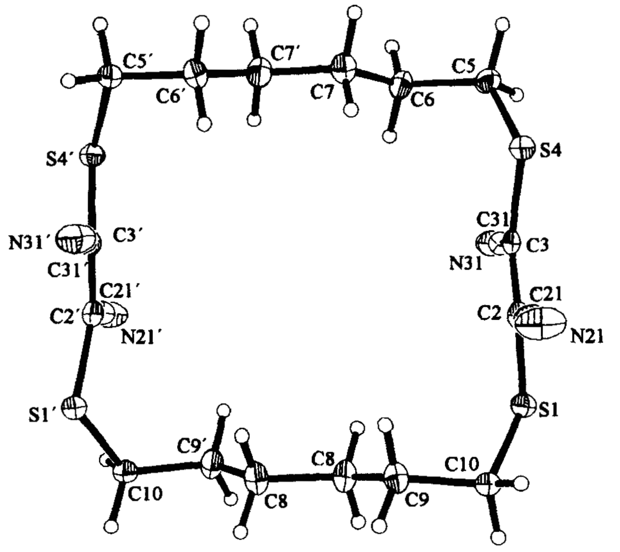


Figure 5 ORTEP illustration of **(E,E)-7**

prisms; m.p.: 159–161°C; R_f: 0.51 (dichloromethane); MS (70eV): m/z(%) = 420 (36) [M^+], 41 (100) [C_3H_5]$^+$; IR (KBr): =2210 cm^{-1} m (C≡N), 1499 m (C=C); UV (chloroform): λ_{max}(lgε) = 278 nm (4.03), 331 (4.43) sh, 341 (4.45); ^{1}H-NMR ($CDCl_3$): δ = 1.59 ppm (m, 4H, CH_2), 1.76 (m, 8H, $SCH_2C\textit{H}_2$), 3.20 (m, 8H, SCH_2); ^{13}C-NMR ($CDCl_3$): δ = 25.5 ppm (CH_2); 29.0 ($SCH_2\textit{C}H_2$); 35.5 (SCH_2); 112.1 (C≡N); 121.4 (C=C); $C_{18}H_{20}N_4S_4$(420.64); Calcd.: C 51.40 H 4.79 N 13.32 S 30.49; Found: C 51.09 H 4.78 N 13.30 S 30.50; **(Z,E)-6**: yield: 1.26 (10%), pale yellow prisms; m.p.: 152–154°C; R_f: 0.62 (dichloromethane); MS (70eV): m/z(%) = 420 (65) [M^+], 69 (100) [(C_5H_9)]$^+$; IR (KBr): =2225 cm^{-1} m, 2210 m (C≡N), 1504 m (C=C); UV (chloroform): λ_{max}(lgε) = 278 (3.54) sh, 345 (4.28), 373 (4.08) sh; ^{1}H-NMR ($CDCl_3$): δ = 1.59 ppm (m), 1.74 (m), 1.89 (p) (0.72:1:0.10) (12H, CH_2); 3.09 (m, 7H, SCH_2); 3.40 (t, 1H, SCH_2); ^{13}C-NMR ($CDCl_3$): δ = 25.9 ppm, 26.8, 26.9, 27.0, 27.1, 28.8, 29.0, 29.1, 29.2, 29.5, 29.9, 30.4, 31.9, 33.1, 34.1, 34.3, 34.4, 34.5, 34.8, 35.0 (0.77:0.11:0.12:0.13:0.04:0.94:0.10:0.11:0.14:0.89:0.91: 0.23:0.12:0.11:0.24:0.10:0.14:1:0.10:0.69) (CH_2); 111.6, 111.7, 111.9, 112.0 (0.98:0.28:0.40:1) (C≡N); 120.8, 121.0, 121.2, 121.9, 122.1, 122.4, 124.6 (0.10:0.11:0.10:0.07:0.84:1:0.34) (C=C); $C_{18}H_{20}N_4S_4$ (420.64); Calcd.: C 51.40 H 4.79 N 13.32 S 30.49; Found: C 51.28 H 4.75 N 13.25 S 30.30; **(E,E)-6**: yield: 0.25 g (2%), colorless needles; m.p.: 206–208°C; R_f: 0.63 (dichloromethane); MS (70eV): m/z(%) = 420 (26) [M^+], 41 (100) [C_3H_5]$^+$; IR (KBr): =2227 cm^{-1} m, 2210 w (C≡N); 1523 w (C=C); UV (chloroform): λ_{max}(lgε) = 358 (4.23) nm, 383 (4.20) sh; ^{1}H-NMR ($CDCl_3$): δ = 1.65 ppm (m, 12H, CH_2), 3.03 (m, 8H, SCH_2); ^{13}C-NMR ($CDCl_3$): δ = 26.0 ppm (CH_2); 30.5 ($SCH_2\textit{C}H_2$); 34.1 (SCH_2); 111.9 (C≡N); 124.6 (C=C); $C_{18}H_{20}N_4S_4$(420.64); Calcd.: C 51.40 H 4.79 N 13.32 S 30.49; Found: C 51.17 H 4.80 N 13.28 S 30.19.

Table 7 Selected torsion angles [deg.] for **(E,E)-7**

C10-S1-C2-C3	−155.7(3)	S1-C2-C3-C31	6.3(4)
S1-C2-C3-S4	−169.0(2)	S4-C3-C2-C21	4.7(5)
C2-C3-S4-C5	−169.4(3)		
C3-S4-C5-C6	69.7(3)	C21-C2-C3-C31	−179.9(4)
S4-C5-C6-C7	55.3(4)		
C5-C6-C7-C7'	179.1(3)	C10-S1-C2-C21	30.5(3)
C6-C7-C7'-C6'	167.8(3)	C5-S4-C3-C31	15.3(3)
C8'-C8-C9-C10	174.5(3)		
C8-C9-C10-S1	56.6(4)		

Cyclization of **(Z)-3** with 1,6-dibromohexane: (Z,Z)-1,4,11,14-Tetrathiacycloeicos-2,12-diene-2,3,12,13-tetracarbonitrile **(Z,Z)-7**: yield: 0.81 g (6%), colorless prisms; m.p.: 166–168°C; R_f: 0.60 (dichloromethane); MS (70eV): m/z(%) = 448 (91) [M^+] 55 (100) [C_4H_7]$^+$; IR (KBr): =2221 cm^{-1} s, 2210 s (C≡N); 1509 s (C=C); UV (chloroform): λ_{max}(lgε) = 278 nm (3.85) sh, 331 (4.39) sh, 342 (4.43); ^{1}H-NMR ($CDCl_3$): δ = 1.43 ppm (m, 8H, CH_2), 1.66 (m, 8H, $SCH_2C\textit{H}_2$); 3.10 (t, 8H, SCH_2); ^{13}C-NMR ($CDCl_3$): δ = 27.7 ppm (CH_2); 30.5 ($SCH_2\textit{C}H_2$); 35.5 (SCH_2); 112.4 (C≡N); 123.1 (C=C); $C_{20}H_{24}N_4S_4$ (448.70); Calcd.: C 53.54 H 5.39 N 12.49 S 28.58; Found: C 53.53 H 5.35 N 12.46 S 28.56; **(Z,E)-7**: yield: 0.94 g (7%), colorless prisms; m.p.: 111–112°C; R_f: 0.66 (dichloromethane); MS (70eV): m/z(%) = 448 (98) [M^+] 55 (100) [C_4H_7]$^+$; IR (KBr): = 2223 cm^{-1} m, 2209 m (C≡N); 1508 m (C=C); UV (chloroform): λ_{max}(lgε) = 278 nm (3.65) sh, 343 (4.35), 375 (3.98) sh; ^{1}H-NMR ($CDCl_3$): δ = 1.45 ppm (m, 8H, CH_2), 1.67 (m, 8H, $SCH_2C\textit{H}_2$), 3.03–3.16 (2m, 8H, SCH_2); ^{13}C-NMR ($CDCl_3$): δ = 27.7 ppm, 27.8, 27.9, 28.2 (0.80:0.97:1:0.25) (CH_2); 30.1, 30.6, 30.8, 30.9 (0.99:0.88:1:0.26) ($SCH_2\textit{C}H_2$); 34.8, 34.9, 35.4, 35.6

(0.24:1:0.95:0.66) (SCH_2); 112.0, 112.4, 112.6 (1:0.92:0.94) (C≡N); 122.6, 123.3, 123.5 (0.93:0.64:1) (C=C); $C_{20}H_{24}N_4S_4$ (448.70); Calcd.: C 53.54 H 5.39 N 12.49 S 28.58; Found: C 53.65 H 5.41 N 12.45 S 28.49. **(E,E)-7**: yield: 0.27 g (2%), yellow prisms; m.p.: 200–202°C; R_f: 0.76 (dichloromethane); MS (70eV): m/z(%) = 448 (59) $[M^+]$ 55 (100) $[C_4H_7]^+$; IR (KBr): = 2225 cm^{-1} m (C≡N); 1500 w (C=C); UV (chloroform): $\lambda_{max}(\lg\epsilon)$ = 365 nm (4.30); ^{1}H-NMR ($CDCl_3$): δ = 1.47 ppm (m, 8H, CH_2), 1.68 (m, 8H, SCH_2CH_2), 3.05 (t, 8H, SCH_2); ^{13}C-NMR ($CDCl_3$): δ = 27.8 ppm (CH_2); 30.5 (SCH_2CH_2); 34.5 (SCH_2); 111.7 (C≡C); 122.4 (C=C); $C_{20}H_{24}N_4S_4$ (448.70); Calcd.: C 53.54 H 5.39 N 12.49 S 28.58; Found.: C 53.36 H 5.30 N 12.53 S 28.51.

Preparation of (E,E)-7:

3.19 g (17.1 mmol) (E)-disodium-1,2-dicyanoethene-1,2-dithiolate **(E)-3** was added to a solution of 4.18 g (17.1 mmol) 1,6-dibromohexane in 390 mL dioxane under an argon atmosphere, protected from light. The reaction suspension was refluxed with stirring for 50 h. Then the mixture was filtered and the solvent was destilled off in vacuo. The residue was taken up in chloroform and keep for several hours in the refrigerator. The precipitated **(E,E)-7** was filtrated off, washed with chloroform and recrystallized from dichloromethane/-hexane. Yield: 0.62 g (8%).

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