Sulfanyl-Substituted [3]Cumulenes and Buta-1,3-dienes from a Tetrakis(pyridinium)-Substituted Butadiene

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Abstract: Treatment of perchlorobuta-1,3-diene with 4-(*N*,*N*-dimethylamino)pyridine resulted in the formation of 1,1′,1″,1‴-(2,3-dichlorobuta-1,3-diene-1,1,4,4-tetrayl)tetrakis[4-(dimethylamino)pyridinium] tetrachloride (structure confirmed by X-ray analysis), which was converted into persulfurated butatrienes ([3]cumulenes), pentakis(sulfanyl)-substituted buta-1,3-dienes, or tetrakis(sulfanyl)-substituted 2,3-dichlorobuta-1,3-dienes by reactions with thiolates or a sulfinate. The outcome of the reaction depends on the reaction conditions and the substitution pattern of the starting sulfur nucleophiles.

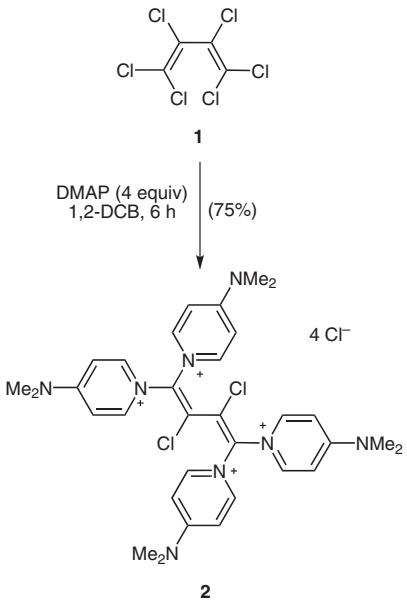
Key words: dienes and trienes, sulfides, pyridines, perchlorinated compounds, persulfurated compounds

Currently, considerable attention is paid to compounds with high sulfur content as they play a crucial role in materials chemistry, supramolecular chemistry, polymer chemistry, nanochemistry, and biochemistry. A review summarizing the syntheses and properties of persulfurated aromatic compounds appeared recently.[1] In materials chemistry, persulfurated compounds are used as electronic conductors,[2] organic ferromagnets,[3] single-molecule magnets,[4] multivalent conducting and magnetic materials,[5] electron-accepting supramolecules,[6] optical materials,[7] and multifunctional[8] as well as electrophotographic materials.[9] Ligands possessing persulfurated benzene cores for metal sensing devices have been developed.[10] In polymer chemistry, they have found interest as stabilizers[1] or, very recently, as high-refractive-index and transparent polymers.[11] Some compounds have been developed as efficient catalysts in the synthesis of gold nanoparticles.[12] The biological relevance of persulfurated compounds is demonstrated by work dealing with the syntheses of analogues of the C-cluster of *Carboxydothermus hydrogenoformans* carbon monoxide dehydrogenase[13] or reactivity analogues of biotin synthase and other members of the *S*-adenosylmethionine enzyme family.[14] With respect to this, butatrienes and butadienes with high sulfur content constitute a hitherto underexploited class of compounds,[15] although they can serve as starting materials for new sulfanyl-substituted butadienes,[16] functionalized thiophenes,[17] and 1,2-dithiins.[18]

In our previous work, 4-(dimethylamino)pyridinium rings proved to be highly versatile ligands for the stabilization of reactive species[19] or for the activation of various substrates toward substitution reactions. Thus, 4-(dimethylamino)pyridinium-substituted heteroaromatics such as pyridine can be used for the synthesis of a broad variety of functionalized pyridines.[20] We describe here an efficient synthesis of sulfanyl-substituted butatrienes ([3]cumulenes) and butadienes, which avoids potentially explosive starting materials or time-consuming syntheses of starting materials. Our synthesis starts from a tetrakis[4-(dimethylamino)pyridinium]-substituted 2,3-dichlorobuta-1,3-diene, which is readily available on reaction of commercially available hexachlorobutadiene and 4-(*N*,*N*-dimethylamino)pyridine.

Thus, reaction of hexachlorobuta-1,3-diene (**1**) with an excess of 4-(*N*,*N*-dimethylamino)pyridine in 1,2-dichlorobenzene (1,2-DCB) at reflux temperature gave the target starting material 1,1′,1″,1‴-(2,3-dichlorobuta-1,3-diene-1,1,4,4-tetrayl)tetrakis[4-(dimethylamino)pyridinium] tetrachloride (**2**) in 75% yield as a yellow solid (Scheme 1).

The ^{1}H NMR spectra of **2** show two different types of heteroaromatic ring systems. In agreement with the proposed



Scheme 1 Synthesis of the starting material

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structure, the HMBC (^1H–^{13}C) spectrum displays all the expected long-range C–H couplings. Single crystals of **2** suitable for an X-ray single-crystal analysis were obtained by slow evaporation of a saturated solution in acetonitrile–methanol (95:5). The substance crystallized with one molecule of hydrogen chloride, in addition to water of crystallization. The molecular drawing is shown in Figure 1. The twisted buta-1,3-diene core adopts an *s-trans* conformation. The dihedral angle Cl–C2–C3–Cl was determined to be 67.7(7)°. The bond lengths of C1–C2 and C3–C4 of the butadiene are identical, and were determined to be 133.4(7) pm. The bond C2–C3 has a length of 147.3(7) pm. The pyridinium rings are twisted out of planarity. The pyridinium rings in the *Z*- and *E*-positions at C1 adopt torsion angles of 59.7(7)° and –128.8°, respectively, whereas those at C4 have dihedral angles of 51.8(7)° (*Z*) and –131.6(7)° (*E*). The intramolecular hydrogen bond linkages [C7–H7···Cl7 375.0(1) pm, C9–H9···Cl6 333.8(3) pm, C19–H19···Cl5 337.3(3) pm, C34–H34···Cl3 380.5(7) pm; crystallographic numbering] between the pyridine rings and chloride counter anions lead to the formation of ion pairs that correspond to a formula unit of $[C_{32}H_{40}Cl_2N_8]Cl_4$. These ion pairs are further linked into a three-dimensional supramolecular structure by intermolecular O–H···Cl and O–H···O hydrogen bonds. The hydrogen bond distances between the oxygen atoms of the water molecules and the chloride ions range from 305.2 to 331.4 pm, the O–H···Cl angles from 156.6 to 176.4°. The hydrogen bond distances O–H···O between the water molecules range from 274.2 to 285.4 pm, and the O–H···O angles range from 155.6 to 166.6°.

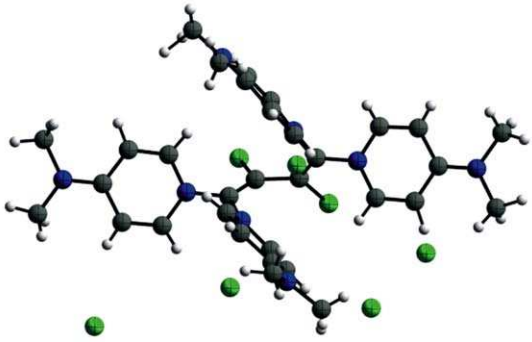
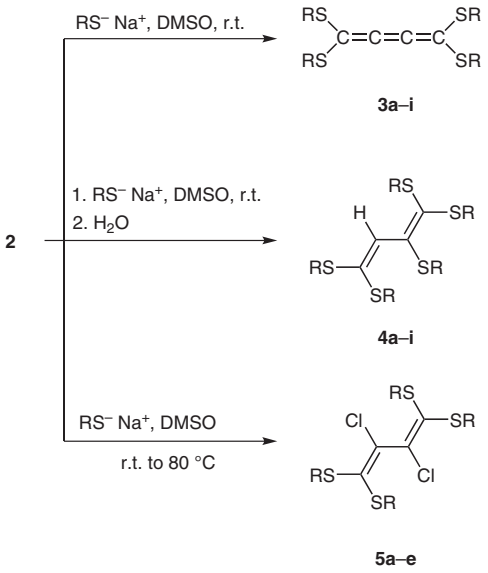


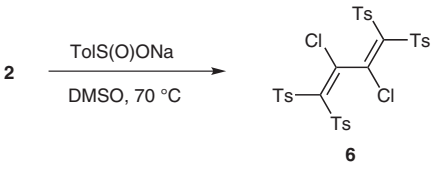
Figure 1 Molecular drawing of butadiene **2**

Reaction of the pyridinium salt **2** with an excess of the appropriate thiolate in anhydrous dimethyl sulfoxide resulted in the smooth formation of the persulfurated [3]cumulenes **3a–i** in reasonable to high yields in one step at room temperature (Scheme 2, Table 1, entries 1–9). Various bases, including triethylamine, potassium *tert*-butoxide, sodium methoxide, *n*-butyllithium, and sodium amide, were screened for preparing the thiolates from the corresponding thiols. The best results were obtained with sodium amide. When starting material **2** is used, the formation of mixtures of mono- and disubstituted butadienes is obviously avoided, whereas these are formed when perchlorobutadiene is used.[21] The [3]cumulenes **3a–c** were previously prepared from buta-1,3-diyne-1,4-diyldilithium – available from 1,4-dichlorobut-2-yne via the potentially explosive buta-1,3-diyne[22] – with electrophilic dichalcogenides RSSR.[18] The *tert*-butyl-, cyclohexyl-, benzyl-, and phenyl derivatives **3d–g** were earlier synthesized starting from tetrachlorobut-1-en-3-yne in 36–62% yields.[23,24] This perchlorobutenyne, however, must be prepared from perchlorobutadiene and butyllithium in low yield,[25] or from 1,1,3,3,4,4-hexachlorobut-1-ene,[26] pentachlorobutadiene,[26] or other chlorinated precursors.[26,27] In some cases, mixtures of compounds are formed by this procedure.[28] An exception is the *tert*-butyl derivative **3d**, which is also formed from perchlorobutadienes with sodium 2-methylpropane-2-thiolate.[21]



Scheme 2 Formation of [3]cumulenes and butadienes from **2**

Sodium *p*-toluenesulfinate reacted with **2** to provide the 2,3-dichlorobuta-1,3-diene **6** in 72% yield (Scheme 3).



Scheme 3 Formation of a 2,3-dichloro-1,1,4,4-tetrasulfonyl-substituted butadiene

When the reaction mixture for the formation of **3a** (R = Me) is quenched with aqueous dimethyl sulfoxide, a spontaneous addition of methanethiol to the central double bond of the butatriene occurs to give the pentakis(methylsulfanyl)-substituted buta-1,3-diene **4a** in excellent yield (81%) (Scheme 2, Table 1, entry 10). Similarly, we prepared, as examples, **4b**,**c** and **4e–h** by this known procedure[21] (entries 11, 12, and 14–17). The *tert*-butyl-substituted cumulene **3d** is inert, so that synthe-

Table 1 Synthesis of [3]Cumulenes **3a–i** and Butadienes **4a–i** and **5a–e**[a]

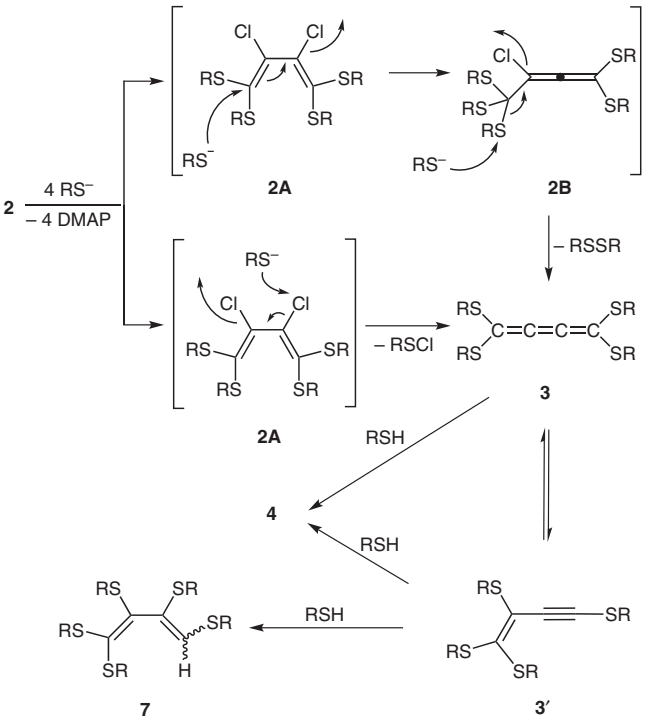
Entry	Product	R	Yield[b] (%)
1	**3a**	Me	75
2	**3b**	Et	72
3	**3c**	*i*-Pr	67
4	**3d**	*t*-Bu	83
5	**3e**	*c*-Hex	74
6	**3f**	Bn	63
7	**3g**	Ph	57
8	**3h**	3-$MeOC_6H_4$	87
9	**3i**	CH_2CO_2Me	47
10	**4a**	Me	81
11	**4b**	Et	77
12	**4c**	*i*-Pr	41
13	**4d**	*t*-Bu	0
14	**4e**	*c*-Hex	67
15	**4f**	Bn	79
16	**4g**	Ph	77
17	**4h**	3-$MeOC_6H_4$	81
18	**4i**	CH_2CO_2Me	0
19	**5a**	4-pyridyl	66
20	**5b**	Ac	51
21	**5c**	$C(=S)NEt_2$	79
22	**5d**	C(=S)OEt	67
23	**5e**	3-methylimidazol-2-yl	53

[a] Reagents and conditions: RS^-Na^+, DMSO, r.t. (**3a–i**, **4a–i**, **5a**,**c**) or 50–80 °C (**5b**,**d**,**e**).
[b] Yields of pure, isolated products.

sis of **4d** failed (entry 13). Under analogous reaction conditions, **4i** decomposed (entry 18).

To the best of our knowledge, only three examples of buta-1,3-dienes with the 2,3-dichloro-1,1,4,4-tetrasulfanyl substitution pattern have been described to date.[17,21,29] The butadiene **5a**, which is a new example, is the main product of the reaction of pyridine-4-thiol with the tetracation **2** in the presence of sodium methoxide (Scheme 2; Table 1, entry 19). The NMR spectra of **5a** clearly show two distinct types of pyridine rings, and a symmetric molecule, as only eight resonance frequencies are detected by ^{13}C NMR spectroscopy. The reactions of **2** with sodium thioacetate required higher temperatures and yielded **5b** (Table 1, entry 20). Compounds **5c**,**d** were obtained in reasonable yields by this procedure (entries 21 and 22) starting from the sodium salt of diethylcarbamodithioic acid and potassium *O*-ethylcarbonodithioate, respectively. The imidazole derivative **5e** was prepared by the reaction of sodium *N*-methylimidazole-2-thiolate with **2** at 60 °C (entry 23). The ^1H and ^{13}C NMR spectra show two different types of imidazole rings. Mass spectra as well as elemental analyses of **5a–e** confirm two chlorine atoms in the molecules.

The reactions leading to the [3]cumulenes must involve a reduction of the starting material **2**, for which two mechanisms can be envisaged: Sequential nucleophilic substitution of the 4-(dimethylamino)pyridinium ligands by the thiolates is supposed to proceed by an addition–elimination mechanism and to result in the butadiene **2A** (Scheme 4). On the one hand, attack of an additional thiolate at position 1 of **2A** in an S_N2'-type reaction can result in the formation of allene **2B**, with chloride as the leaving group. Attack of a second thiolate on the sulfur atom of a sulfanyl substituent can then give a disulfide by oxidation and concomitant reduction of **2B** to form butatriene **3**. Indeed, a 1:1 ratio of either methanethiolate and *tert*-butanethiolate, or ethanethiolate and *tert*-butanethiolate, respectively, resulted in the formation of a mixture of compounds, from which an adduct such as intermediate **2B** was identified as a peak at $m/z = 402$ and $m/z = 416$, respectively. On the other hand, attack of the thiolate on the chlorine substituent at position 2 of the butadiene **2A** can result in the formation of butatriene **3**, chloride, and the alkanesulfenyl chloride (RSCl). This could react with excess thiolate to give a disulfide and chloride. We isolated, in accordance with either pathway, disulfides such as diphenyl disulfide, di-*tert*-butyl disulfide, dibenzyl disulfide, and dicyclohexyl disulfide in good yields. The spec-



Scheme 4 Proposed mechanisms

tra showed no hint of the formation of but-1-en-3-yne **3′**. It was proposed earlier for related systems that the interconversion of **3/3′** is reversible when proton-donating agents are absent.[24] In agreement with the proposed structures **4**, the gs-HMBC (^{1}H–^{13}C) spectra display all expected long-range C–H couplings for the olefinic proton. The HMBC correlation shows a $^4J_{CH}$ coupling with one, and a $^3J_{CH}$ coupling with two carbon atoms. Thus, the alternative structure **7** was excluded from consideration.

In summary, we present an easy access to persulfurated [3]cumulenes and sulfanyl-substituted buta-1,3-dienes starting from 4-(*N*,*N*-dimethylamino)pyridine and commercially available perchlorobutadiene. The method described here broadens the interesting synthetic applicability of polyhetarenium salts developed by Streitwieser,[30] Weiss,[31] and our group.[19,20]

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 and Avance DPX-200 spectrometers. The internal standard was TMS for measurements of samples as solns in $CDCl_3$ and D_2O. FT-IR spectra were obtained on a Bruker Vektor 22 in the range 400–4000 cm^{-1}. Solids were prepared as pellets (2.5%) in KBr and oils were prepared as films on NaCl plates. The mass spectra were measured with a Hewlett Packard HP 5989 instrument. The ESI mass spectra were measured with an Agilent LCMSD series HP 1100 instrument with APIES. Melting points are uncorrected and were determined on an apparatus according to Dr. Tottoli (Büchi). Yields are not optimized.

1,1′,1″,1‴-(2,3-Dichlorobuta-1,3-diene-1,1,4,4-tetrayl)tetrakis[4-(dimethylamino)pyridinium] Tetrachloride (2)

Hexachlorobuta-1,3-diene (**1**; 1.04 g, 4 mmol) was dissolved in 1,2-dichlorobenzene (100 mL), and DMAP (1.20 g, 10 mmol) was then added. After the mixture had been kept at reflux temperature for 6 h, a solid precipitated, which formed a yellow solid after recrystallization from MeCN–MeOH (95:5).

Yield: 2.71 g (75%); mp 235–238 °C (dec).

IR (KBr): 3406, 3055, 1644, 1586, 1406, 1211, 1161, 828 cm^{-1}.

^{1}H NMR (400 MHz, D_2O): δ = 8.06 (d, *J* = 7.8 Hz, 4 H, αH), 7.99 (d, *J* = 7.8 Hz, 4 H, αH), 7.18 (d, *J* = 7.8 Hz, 4 H, βH), 7.08 (d, *J* = 7.8 Hz, 4 H, βH), 3.40 (s, 12 H, NMe_2), 3.37 (s, 12 H, NMe_2).

^{13}C NMR (100 MHz, D_2O): δ = 157.2 (2 C), 156.9 (2 C), 139.5 (4 C), 139.4 (4 C), 137.5 (2 C), 119.9 (2 C), 109.7 (4 C), 108.7 (4 C), 41.0 (4 C), 40.7 (4 C).

ESI-MS: *m*/*z* [M + 3Cl$^-$]$^+$ = 712.8.

Anal. Calcd for $C_{32}H_{40}Cl_6N_8 \cdot 9H_2O$: C, 42.10; H, 6.41; N, 12.29. Found: C, 41.73; H, 5.95; N, 12.20.

X-ray Crystal Structure Analysis of 2

A suitable single crystal of the title compound was selected under a polarization microscope and mounted in a glass capillary (*d* = 0.5 mm). The crystal structure was determined by X-ray diffraction analysis using graphite monochromated Mo Kα radiation (0.71073 Å) [*T* = 223(2) K], whereas the scattering intensities were collected with a single-crystal diffractometer (STOE IPDS II). The crystal structure was solved by direct methods using SHELXS-97 and refined using alternating cycles of least squares refinements against *F*2 (SHELXL-97).[32] All non-hydrogen atoms were located in difference Fourier maps and were refined with anisotropic displacement parameters. The hydrogen positions were determined by a final difference Fourier synthesis. The hydrogen atom of HCl could not be located.

Crystal structure data for compound **2**: $C_{64}H_{118}Cl_{13}N_{16}O_{18}$, chemical formula weight 1860.59 g·mol^{-1}, space group *P*1 (triclinic), *a* = 9.549(1) Å, *b* = 13.726(2) Å, *c* = 17.619(2) Å, α = 94.58(1)°, β = 91.30(1)°, γ = 101.11(1)°, *V* = 2257.1(5) Å^3, *Z* = 1, D_C = 1.369 g·cm^{-3}, *F*(000) = 979, 7894 independent reflections, 734 parameters, *R*1 = 0.0526, *wR*2 = 0.1371 [$I > 2\sigma(I)$], goodness-of-fit on *F*2 = 1.042, residual electron density 0.395 and –0.844 e Å^{-3}. CCDC 710964 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Buta-1,2,3-trienes 3a–d; General Procedure

The salt **2** (0.454 g, 0.5 mmol) was dissolved in anhyd DMSO (15 mL). A soln of the appropriate sodium thiolate (3 mmol) in DMSO (10 mL) was added dropwise over 15 min under N_2. The reaction mixture was then filtered through silica gel and extracted with CH_2Cl_2 (3 × 35 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated in vacuo to give dark oils. Flash chromatography (silica gel, PE–EtOAc) afforded the products.

1,1,4,4-Tetrakis(methylsulfanyl)butatriene (3a)

A soln of NaSMe (0.21 g, 3 mmol) in DMSO (10 mL) was added to a soln of the salt **2**. After column chromatography (silica gel, PE–EtOAc, 20:1) a yellow oil was obtained.

Yield: 88 mg (75%).

All data are in agreement with those published earlier.[18]

Anal. Calcd for $C_8H_{12}S_4$: C, 40.64; H, 5.12. Found: C, 41.01; H, 5.03.

1,1,4,4-Tetrakis(ethylsulfanyl)butatriene (3b)

NaSEt (0.25 g, 3 mmol) gave **3b** as a yellow oil after chromatography (PE–EtOAc, 20:1).

Yield: 105 mg (72%).

All data are in agreement with those published earlier.[18]

Anal. Calcd for $C_{12}H_{20}S_4$: C, 49.27; H, 6.89. Found: C, 48.93; H, 6.67.

1,1,4,4-Tetrakis(isopropylsulfanyl)butatriene (3c)

NaS*i*-Pr (0.3 g, 3 mmol) gave **3c** as a yellow oil after chromatography (PE–EtOAc, 20:1).

Yield: 116 mg (67%).

All data are in agreement with those published earlier.[18]

Anal. Calcd for $C_{16}H_{28}S_4$: C, 55.12; H, 8.09. Found: C, 54.46; H, 8.01.

1,1,4,4-Tetrakis(*tert*-butylsulfanyl)butatriene (3d)

This compound has been mentioned before in the literature, but was not characterized completely.[23,24]

NaS*t*-Bu (0.34 g, 3 mmol) gave **3d** as yellow crystals after chromatography (PE–EtOAc, 20:1).

Yield: 168 mg (83%); mp 170–171 °C (Lit.[23,24] 170–171 °C).

IR (KBr): 2959, 2919, 1557, 1453, 1162 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.45 (s, 36 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.8, 107.4, 49.3, 30.8.

MS (EI, 70 eV): *m*/*z* (%) = 404 [M$^+$] (85).

Anal. Calcd for $C_{20}H_{36}S_4$: C, 59.35; H, 8.96. Found: C, 59.41; H, 8.74.

Buta-1,2,3-trienes 3e–i; General Procedure

$NaNH_2$ (0.156 g, 4 mmol) was dissolved in anhyd MeCN (15 mL) at r.t., and the appropriate thiol RSH (4 mmol) was added in one portion. The mixture was then stirred for 3 h. The precipitate was collected by filtration, washed several times with anhyd Et_2O under an inert atmosphere, and dried in vacuo. A sample of the thus formed salt RSNa (3 mmol) was then dissolved in anhyd DMSO (10 mL) and added dropwise to a soln of **2** (0.454 g, 0.5 mmol) within 15 min. The mixture was then filtered through silica gel. The product was finally extracted with CH_2Cl_2 (3 × 35 mL), and the organic layers were combined and dried ($MgSO_4$). The solvent was evaporated and the residue was subjected to column chromatography.

1,1,4,4-Tetrakis(cyclohexylsulfanyl)butatriene (3e)

This compound has been mentioned before in the literature, but was not characterized completely.[23,24]

c-HexSH (0.465 g, 4 mmol) was used. A sample of its salt (0.414 g, 3 mmol) was then reacted with **2**. Chromatographic separation (silica gel, PE–EtOAc, 25:1) gave a colorless solid.

Yield: 188 mg (74%); mp 83–85 °C (Lit.[23,24] 86–87 °C).

IR (KBr): 2933, 2852, 1536, 1447, 1197 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.73–2.61 (m, 4 H), 2.08–2.00 (m, 8 H), 1.81–1.56 (m, 12 H), 1.43–1.22 (m, 20 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 145.6, 106.1, 49.9, 32.8, 26.1, 25.7.

MS (EI, 70 eV): *m*/*z* (%) = 508 [M^+] (100).

Anal. Calcd for $C_{28}H_{44}S_4$: C, 66.08; H, 8.71. Found: C, 65.79; H, 8.83.

1,1,4,4-Tetrakis(benzylsulfanyl)butatriene (3f)

This compound has been mentioned before in the literature, but was not characterized completely.[23,24]

BnSH (0.497 g, 4 mmol) was used to prepare the salt, of which a sample (0.438 g, 3 mmol) was used for the reaction with **2**. Chromatography (silica gel, PE–EtOAc, 15:1) gave **3f**.

Yield: 170 mg (63%); mp 85–87 °C (Lit.[23,24] 86–87 °C).

IR (KBr): 3053, 3027, 2911, 1573, 1453, 1070 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.27 (m, 20 H), 3.59 (s, 8 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 149.2, 137.4, 129.4, 128.5, 127.4, 108.6, 43.3.

MS (EI, 70 eV): *m*/*z* (%) = 540 [M^+] (74).

Anal. Calcd for $C_{32}H_{28}S_4$: C, 71.07; H, 5.22. Found: C, 71.20; H, 5.03.

1,1,4,4-Tetrakis(phenylsulfanyl)butatriene (3g)

NaSPh (0.4 g, 3 mmol) gave **3g** as a yellow solid after purification by chromatography (PE–EtOAc, 15:1).

Yield: 138 mg (57%); mp 100–101 °C (Lit.[23,24] 100–100.5 °C).

All data are in agreement with those published earlier.[23,24]

MS (EI, 70 eV): *m*/*z* (%) = 484 [M^+] (100).

Anal. Calcd for $C_{28}H_{20}S_4$: C, 69.38; H, 4.16. Found: C, 69.50; H, 4.21.

1,1,4,4-Tetrakis(3-methoxyphenylsulfanyl)butatriene (3h)

3-Methoxybenzenethiol (0.56 g, 4 mmol) was used to prepare the salt, of which a sample (0.48 g, 3 mmol) was reacted with **2**. Chromatography (silica gel, PE–EtOAc, 12:1) gave a yellow solid.

Yield: 263 mg (87%); mp 109–111 °C.

IR (NaCl, thin film): 3063, 2961, 1692, 1578, 1556, 1436, 1268 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.22 (t, *J* = 7.2 Hz, 4 H), 7.19–7.08 (m, 8 H), 6.80–6.75 (m, 4 H), 3.78 (s, 12 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 160.0, 146.7, 138.3, 129.9, 119.6, 113.1, 112.6, 107.3, 55.3.

MS (EI, 70 eV): *m*/*z* (%) = 604 [M^+] (80).

Anal. Calcd for $C_{32}H_{28}O_4S_4$: C, 63.55; H, 4.67. Found: C, 63.37; H, 4.42.

Tetramethyl 2,2′,2″,2‴-(Butatriene-1,1,4,4-tetrayltetrasulfanetetrayl)tetraacetate (3i)

$HSCH_2CO_2Me$ (0.425 g, 4 mmol) was used to prepare the salt, of which a sample (0.384 g, 3 mmol) was reacted with **2**. A yellow oil was obtained after chromatographic workup (silica gel, PE–EtOAc, 2:1).

Yield: 110 mg (47%).

IR (NaCl, thin film): 2954, 2845, 1710, 1556, 1436, 1008 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 3.75 (s, 12 H, CH_3), 3.71 (s, 8 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.8, 148.9, 108.4, 52.8, 36.6.

MS (EI, 70 eV): *m*/*z* (%) = 408 [M^+ – 2OMe] (45), 292 [M^+ – 4COOMe] (75).

Anal. Calcd for $C_{16}H_{20}O_8S_4$: C, 41.01; H, 4.30. found: C, 41.43; H, 4.13.

Pentakis(sulfanyl)buta-1,3-dienes 4; General Procedure

The salt **2** (0.454 g, 0.5 mmol) was dissolved in anhyd DMSO (15 mL) and a soln of the appropriate sodium thiolate RSNa (3 mmol) in DMSO (10 mL) was added dropwise within 15 min under an inert gas atmosphere. H_2O (10 mL) was then added. The products were extracted with CH_2Cl_2 (3 × 35 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated to give a dark oil. Flash chromatography (silica gel, PE–EtOAc) afforded the products.

1,1,2,4,4-Pentakis(methylsulfanyl)buta-1,3-diene (4a)

A soln of NaSMe (0.28 g, 4 mmol) in DMSO (10 mL) was used. After column chromatography (silica gel, PE–EtOAc, 20:1) a yellow oil was obtained.

Yield: 115 mg (81%).

IR (NaCl, thin film): 2985, 2917, 1560, 1430, 444 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 6.13 (s, 1 H, =CH), 2.39 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.8, 139.1, 128.8, 123.9, 17.6, 17.2, 17.0, 16.4, 16.3.

MS (EI, 70 eV): *m*/*z* (%) = 284 [M^+] (100).

Anal. Calcd for $C_9H_{16}S_5$: C, 37.99; H, 5.67. Found: C, 37.73; H, 5.87.

1,1,2,4,4-Pentakis(ethylsulfanyl)buta-1,3-diene (4b)

This compound has been mentioned before in the literature, but was not characterized completely.[28]

A soln of NaSEt (0.33 g, 4 mmol) in DMSO (10 mL) was used. After column chromatography (silica gel, PE–EtOAc, 20:1) a yellow oil was obtained.

Yield: 136 mg (77%).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.2, 136.5, 129.9, 127.6, 28.5, 28.4, 27.8, 27.5 (2 C), 15.3, 15.2, 15.1, 14.9, 14.7.

MS (EI, 70 eV): *m*/*z* (%) = 354 [M^+] (100).

Anal. Calcd for $C_{14}H_{26}S_5$: C, 47.41; H, 7.39. Found: C, 47.72; H, 7.18.

1,1,2,4,4-Pentakis(isopropylsulfanyl)buta-1,3-diene (4c)
A soln of NaS*i*-Pr (0.4 g, 4 mmol) in DMSO (10 mL) was used. After column chromatography (silica gel, PE–EtOAc, 20:1) a yellow oil was obtained.

Yield: 0.087 g (41%).

IR (NaCl, thin film): 2954, 2895, 1561, 1430 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 6.45 (s, 1 H, =CH), 3.73–3.26 (m, 5 H, CH), 1.36–1.25 (m, 30 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.9, 134.7, 130.5, 127.7, 41.6, 41.3, 39.2, 38.9, 23.3, 23.2, 23.0, 22.6, 22.3, 21.9.

MS (EI, 70 eV): *m*/*z* (%) = 424 [M^+] (100).

Anal. Calcd for $C_{19}H_{36}S_5$: C, 53.72; H, 8.54. Found: C, 53.51; H, 8.13.

1,1,2,4,4-Pentakis(cyclohexylsulfanyl)buta-1,3-diene (4e)
This compound has been mentioned before in the literature, but was not characterized completely.[24]

$NaNH_2$ (0.156 g, 4 mmol) was added to anhyd MeCN (15 mL) at r.t. and *c*-HexSH (0.47 g, 4 mmol) was added in one portion. The mixture was stirred for 3 h. The precipitate was collected by filtration, washed several times with anhyd Et_2O under N_2, and dried in vacuo. This salt was then dissolved in DMSO (10 mL) and added to a soln of **2** (0.454 g, 0.5 mmol). The product was extracted with CH_2Cl_2 (3 × 35 mL) after quenching with H_2O. The organic layers were combined and dried ($MgSO_4$). Finally, the solvent was evaporated and the resulting residue was subjected to column chromatography (silica gel, PE–EtOAc, 25:1); this gave a yellow oil.

Yield: 209 mg (67%).

MS (EI, 70 eV): *m*/*z* (%) = 624 [M^+] (80).

Anal. Calcd for $C_{34}H_{56}S_5$: C, 65.32; H, 9.03. Found: C, 64.97; H, 9.34.

1,1,2,4,4-Pentakis(benzylsulfanyl)buta-1,3-diene (4f)
$NaNH_2$ (0.156 g, 4 mmol) was added to anhyd MeCN (15 mL) at r.t. and BnSH (0.49 g, 4 mmol) was added in one portion. The mixture was then stirred for 3 h. The precipitate was collected by filtration, washed several times with anhyd Et_2O under N_2, and dried in vacuo. This salt was then dissolved in DMSO (10 mL) and added to a soln of **2** (0.454 g, 0.5 mmol). H_2O (10 mL) was added, and then the product was extracted with CH_2Cl_2 (3 × 35 mL). The organic layers were combined, dried ($MgSO_4$), and evaporated, and the resulting residue was subjected to column chromatography (silica gel, PE–EtOAc, 15:1); this gave a yellow oil.

Yield: 262 mg (79%).

IR (NaCl, thin film): 3060, 3027, 2920, 1601, 1494, 1236, 766 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.34–7.08 (m, 25 H, Ph), 5.73 (s, 1 H, =CH), 4.05 (s, 2 H, CH_2), 3.91 (s, 2 H, CH_2), 3.82 (s, 2 H, CH_2), 3.78 (s, 2 H, CH_2), 3.28 (s, 2 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.2, 138.1, 137.9, 137.8, 137.7, 137.3, 136.2, 130.5, 130.2, 129.3, 129.1, 129.04, 129.01, 128.8, 128.6, 128.5, 128.4, 128.3, 127.7, 127.3, 127.2, 127.0, 126.9, 126.8, 39.1, 38.6, 38.1, 37.9, 37.4.

MS (EI, 70 eV): *m*/*z* (%) = 573 [M^+ – benzyl] (65), 451 (36).

Anal. Calcd for $C_{39}H_{36}S_5$: C, 70.44; H, 5.46. Found: C, 70.21; H, 5.72.

1,1,2,4,4-Pentakis(phenylsulfanyl)buta-1,3-diene (4g)
This compound has been mentioned before in the literature, but was not characterized completely.[24]

A soln of NaSPh (0.53 g, 4 mmol) in DMSO (10 mL) was used. After column chromatography (silica gel, PE–EtOAc, 20:1) yellow crystals were obtained.

Yield: 229 mg (77%); mp 77–78 °C (Lit.[24] 78–79 °C).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.3, 137.8, 134.7, 134.0, 133.4, 132.8, 132.7, 132.6, 132.4, 131.2, 130.9, 129.7, 129.0, 128.7, 128.6, 128.3, 128.0, 127.6, 127.5, 127.1, 127.0 (some signals overlap).

Anal. Calcd for $C_{34}H_{26}S_5$: C, 68.64; H, 4.41. Found: C, 68.43; H, 4.19.

1,1,2,4,4-Pentakis(3-methoxyphenylsulfanyl)buta-1,3-diene (4h)
$NaNH_2$ (0.156 g, 4 mmol) was dissolved in anhyd MeCN (15 mL) at r.t. and 3-methoxybenzenethiol (0.56 g, 4 mmol) was added in a single portion. The mixture was stirred for 3 h. The precipitate was filtered and washed several times with anhyd Et_2O under N_2. The solid was dried under vacuum. The prepared sodium salt was dissolved in DMSO (10 mL) and was added to a soln of **2** (0.454 g, 0.5 mmol). H_2O (10 mL) was added and the adduct was extracted with CH_2Cl_2 (3 × 35 mL). The organic layers were combined and dried ($MgSO_4$). The solvent was evaporated and after column chromatography (silica gel, PE–EtOAc, 10: 1) a yellow oily solid was obtained.

Yield: 301 mg (81%).

IR (NaCl, thin film): 3072, 3001, 2935, 2833, 1589, 1477, 1246, 1039 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.23–6.70 (m, 20 H, aryl), 6.46 (s, 1 H, =CH), 3.78 (s, 3 H, CH_3), 3.70 (s, 3 H, CH_3), 3.67 (s, 6 H, 2 CH_3), 3.63 (s, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 159.7, 159.6, 159.5, 159.3, 142.9, 137.3, 135.8, 135.2, 134.2, 133.9, 133.6, 131.8, 129.7, 129.4, 129.3, 129.1, 125.5, 125.1, 124.6, 123.3, 123.1, 118.0, 117.6, 116.9, 115.7, 115.5, 114.4, 114.2, 114.1, 113.7, 113.4, 55.3, 55.2.

MS (EI, 70 eV): *m*/*z* (%) = 609 [M^+ – $MeOC_6H_4S$] (66), 470 [M^+ – $2MeOC_6H_4S$] (43), 326 (17).

Anal. Calcd for $C_{39}H_{36}S_5$: C, 62.87, H, 4.87. Found: C, 63.05; H, 4.47.

2,3-Dichloro-1,1,4,4-tetrakis(4-pyridylsulfanyl)buta-1,3-diene (5a)
A soln of the salt **2** (0.454 g, 0.5 mmol) was added dropwise to a soln of NaOMe (0.22 g, 4 mmol) and pyridine-4-thiol (0.44 g, 4 mmol) in DMSO (10 mL). The mixture was then stirred for 2 h at r.t. CH_2Cl_2 (3 × 35 mL) was used for extraction, and the organic layers were combined, dried ($MgSO_4$), and concentrated to give a dark oil. Column chromatography (silica gel, PE–EtOAc, 2:1) afforded the product as a yellow oil.

Yield: 184 mg (66%).

IR (NaCl, thin film): 3406, 3034, 1660, 1568, 1405, 803 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 8.55 (dd, *J* = 4.5, 1.6 Hz, 4 H), 8.49 (dd, *J* = 4.5, 1.6 Hz, 4 H), 7.36 (dd, *J* = 4.5, 1.6 Hz, 4 H), 7.25 (dd, *J* = 4.5, 1.6 Hz, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 150.4, 149.9, 146.4, 145.7, 138.7, 124.7, 124.1, 120.8.

ESI-MS: *m*/*z* (%) = 480 [M^+ – pyridine] (100), 481 (25), 482 (65).

Anal. Calcd for $C_{24}H_{16}Cl_2N_4S_4$: C, 51.51; H, 2.88; N, 10.01. Found: C, 52.08; H, 2.36; N, 9.74.

***S*,*S*′,*S*″,*S*‴-2,3-Dichlorobuta-1,3-diene-1,1,4,4-tetrayl Tetraethanethioate (5b)**
$NaNH_2$ (0.156 g, 4 mmol) was dissolved in anhyd MeCN (15 mL) at r.t. and AcSH (0.3 g, 4 mmol) was added in a single portion. The

mixture was stirred for 3 h. The precipitate was collected by filtration, washed several times with anhyd Et_2O under N_2, and dried in vacuo. This salt was then dissolved in DMSO (10 mL) and added to a soln of **2** (0.454 g, 0.5 mmol) and subsequently stirred at 80 °C for 1 h. The product was then extracted with CH_2Cl_2, and the organic layers were combined and dried ($MgSO_4$). Finally, the solvent was evaporated and the resulting residue was subjected to column chromatography (silica gel, PE–EtOAc, 3:1) to give a red solid.

Yield: 107 mg (51%); mp 61–63 °C.

IR (KBr): 2907, 1698, 1567, 1434 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.52 (s, 6 H, CH_3), 2.51 (s, 6 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 191.2, 191.1, 138.2, 117.8, 31.6, 31.5.

MS (EI, 70 eV): *m*/*z* (%) = 418 [M^+] (91).

Anal. Calcd for $C_{12}H_{12}Cl_2O_4S_4$: C, 34.37; H, 2.88. Found: C, 34.21; H, 2.72.

2,3-Dichlorobuta-1,3-diene-1,1,4,4-tetrayl Tetrakis(diethylcarbamodithioate) (5c)

A soln of sodium diethylcarbamodithioate (0.67 g, 3 mmol) in DMSO (10 mL) was added to a soln of the salt **2** (0.454 g, 0.5 mmol). The mixture was then stirred at r.t. for 3 h, and subsequently filtered through silica gel. The product was extracted with CH_2Cl_2 (3 × 35 mL), and the organic layers were combined and dried ($MgSO_4$). Finally, the solvent was evaporated to give a residue, which was subjected to column chromatography (silica gel, PE–EtOAc, 5:1); this gave yellow needles.

Yield: 281 mg (79%); mp 52–53 C.

IR (KBr): 2874, 1702, 1534, 1422 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 4.07–4.01 (m, 8 H), 1.50 (t, *J* = 5.5 Hz, 6 H), 1.32 (t, *J* = 5.5 Hz, 6 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 192.7 (overlapping signals), 138.4, 122.1, 52.1, 47.6, 13.6, 11.5.

MS (EI, 70 eV): *m*/*z* (%) = 566 [M^+ – 2 NEt_2] (77).

Anal. Calcd for $C_{24}H_{40}Cl_2N_4S_8$: C, 40.48; H, 5.66; N, 7.87. Found: C, 40.91; H, 5.32; N, 7.33.

***S*,*S*′,*S*″,*S*‴-2,3-Dichlorobuta-1,3-diene-1,1,4,4-tetrayl *O*,*O*′,*O*″,*O*‴-Tetraethyl Tetrakiscarbonodithioate (5d)**

A soln of potassium *O*-ethylcarbonodithioate (0.3 g, 3 mmol) in DMSO (10 mL) was added to a soln of the salt **2** (0.454 g, 0.5 mmol). The mixture was then stirred at 50 °C for 90 min, and subsequently filtered through silica gel. The product was extracted with CH_2Cl_2 (3 × 35 mL), and the organic layers were combined and dried ($MgSO_4$). Finally, the solvent was evaporated to give a residue which was subjected to column chromatography (silica gel, PE–EtOAc, 5:1); this gave a yellow oily solid.

Yield: 202 mg (67%).

IR (NaCl, thin film): 2893, 1697, 1660, 1548, 1413 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 4.64 (q, *J* = 6 Hz, 4 H), 4.33 (q, *J* = 6 Hz, 4 H), 1.45–1.30 (m, 12 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 215.0, 214.7, 139.3, 118.6, 30.1, 29.6, 13.8, 13.4.

MS (EI, 70 eV): *m*/*z* (%) = 558 [M^+ – OEt] (64).

Anal. Calcd for $C_{16}H_{20}Cl_2O_4S_8$: C, 31.83; H, 3.34. Found: C, 32.12; H, 3.13.

2,3-Dichloro-1,1,4,4-tetrakis[(1-methyl-1*H*-imidazol-2-yl)sulfanyl]buta-1,3-diene (5e)

$NaNH_2$ (0.156 g, 4 mmol) was dissolved in anhyd MeCN (15 mL) at r.t. and 1-methylimidazole-2-thiol (0.459 g, 4 mmol) was added in one portion. The mixture was then stirred for 4 h, before the precipitate was collected by filtration, washed several times with anhyd Et_2O under an inert atmosphere, and dried in vacuo. A portion of this salt (0.41 g, 3 mmol) was then dissolved in anhyd DMSO (20 mL) and added to a soln of **2** (0.454 g, 0.5 mmol). The mixture was stirred at 60 °C for 3 h under N_2, before it was filtered through silica gel. The product was finally extracted with CH_2Cl_2 (3 × 40 mL), and the organic layers were combined and dried ($MgSO_4$). The solvent was evaporated and the residue was subjected to column chromatography (silica gel, PE–EtOAc, 1:1); this gave a yellow solid.

Yield: 151 mg (53%); mp 137–140 °C.

IR (KBr): 3160, 3108, 1572, 1466, 1276 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.03 (d, *J* = 2.3 Hz, 2 H), 6.97 (d, *J* = 2.3 Hz, 2 H), 6.90 (d, *J* = 2.3 Hz, 2 H), 6.84 (d, *J* = 2.3 Hz, 2 H), 3.65 (s, 6 H, CH_3), 3.55 (s, 6 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 160.3, 160.2, 123.4, 121.2, 121.1, 117.4, 115.2, 115.1, 34.6, 34.5.

MS (EI, 70 eV): *m*/*z* (%) = 570 [M^+] (57).

Anal. Calcd for $C_{20}H_{20}Cl_2N_8S_4$: C, 42.03; H, 3.53, N, 19.60. Found: C, 42.51; H, 3.34; N, 19.21.

2,3-Dichloro-1,1,4,4-tetratosylbuta-1,3-diene (6)

A soln of sodium toluene-4-sulfinate (0.54 g, 3 mmol) in DMSO (10 mL) was added to a soln of the salt **2** (0.454 g, 0.5 mmol). The mixture was then stirred at 70 °C for 45 min. The reaction mixture was filtered through silica gel, the product was extracted with CH_2Cl_2 (3 × 35 mL), and the organic layers were combined and dried ($MgSO_4$). Finally, the solvent was evaporated to give a residue which was subjected to column chromatography (silica gel, PE–EtOAc, 10:1); this gave a white solid.

Yield: 266 mg (72%); mp 72–73 °C.

IR (KBr): 3042, 2915, 1590, 1488, 1323, 1291, 1139, 806 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 7.9 Hz, 4 H), 7.24 (d, *J* = 7.9 Hz, 4 H), 7.20 (d, *J* = 7.9 Hz, 4 H), 7.14 (d, *J* = 7.9 Hz, 4 H), 2.42 (s, 6 H, CH_3), 2.38 (s, 6 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.6, 142.0, 140.4, 136.5, 130.2, 129.3, 127.6, 124.6, 21.6, 21.5 (overlapped), 21.5 (overlapped).

ESI-MS: *m*/*z* = 581, 296.

Anal. Calcd for $C_{32}H_{28}Cl_2O_8S_4$: C, 51.96; H, 3.82. Found: C, 52.41; H, 3.43.

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References

(1) Gingras, M.; Raimundo, J.-M.; Chabre, Y. M. *Angew. Chem. Int. Ed.* **2006**, *45*, 1686; *Angew. Chem.* **2006**, *118*, 1718.
(2) Adam, M.; Müllen, K. *Adv. Mater.* **1994**, *6*, 439.
(3) Nakai, T.; Kozaki, M.; Sato, K.; Shiomi, D.; Takui, T.; Itoch, K.; Okada, K. *Chem. Lett.* **1998**, 933.
(4) Hiraga, H.; Miyasaka, H.; Takaishi, S.; Kajiwara, T.; Yamashita, M. *Inorg. Chim. Acta* **2008**, *361*, 3863.
(5) Pointillard, F.; Le Gal, Y.; Golhen, S.; Cador, O.; Ouahab, L. *Inorg. Chem.* **2008**, *47*, 9730.
(6) Mayor, M.; Lehn, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 11231.

(7) Gostevskaya, V. I.; Gavrilova, G. M.; Afonin, A. V.; Amosova, S. V. *Russ. J. Org. Chem.* **2001**, *37*, 388.
(8) Kusamoto, T.; Kume, S.; Nishihara, H. *J. Am. Chem. Soc.* **2008**, *130*, 13844.
(9) Takahiro, F.; Masatoshi, T.; Hirotoshi, K.; Atsuo, O., (Mitsui Chemicals Inc.) JP 267975, **2003**; *Chem. Abstr.* **2003**, *139*, 261164.
(10) Aubert, C.; Dallaire, C.; Gingras, M. *Tetrahedron Lett.* **2008**, *49*, 5355.
(11) You, N.-H.; Suzuki, Y.; Yorifuri, D.; Ando, S.; Ueda, M. *Macromolecules* **2008**, *41*, 6361.
(12) Bergamini, G.; Ceroni, P.; Balzani, V.; Gingras, M.; Raimundo, J. M.; Morandi, V.; Merli, P. G. *Chem. Commun.* **2007**, 4167.
(13) Panda, R.; Berlinguette, C. P.; Zhang, Y.; Holm, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 11092.
(14) Daley, C. J. A.; Holm, R. H. J. *Inorg. Chem.* **2003**, *97*, 287.
(15) Zimmer, R. In *Science of Synthesis*; de Meijere, A., Ed.; Thieme: Stuttgart, **2006**.
(16) Ibiş, C.; Sayil, Ç. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *86*, 55.
(17) Roedig, A.; Zaby, G. *Chem. Ber.* **1980**, *113*, 3342.
(18) Block, E.; Tries, F.; He, C.; Guo, C.; Thiruvazhi, M.; Toscano, P. J. *Org. Lett.* **2003**, *5*, 1325.
(19) (a) Schmidt, A.; Lindner, A.; Ramírez, F. J. *J. Mol. Struct.* **2007**, *834-836*, 311. (b) Schmidt, A.; Mordhorst, T.; Nieger, M. *Synthesis* **2006**, 3987. (c) Schmidt, A.; Lindner, A.; Nieger, M.; Ruiz Delgado, M. C.; Ramírez, F. J. *Org. Biomol. Chem.* **2006**, *4*, 3056. (d) Schmidt, A.; Kobakhidze, N.; Kindermann, M. K. *J. Chem. Soc., Perkin Trans. 1* **2002**, 982.
(20) (a) Schmidt, A.; Mordhorst, T.; Namyslo, J. C.; Telle, W. *J. Heterocycl. Chem.* **2007**, *44*, 679. (b) Schmidt, A.; Namyslo, J. C.; Mordhorst, T. *Tetrahedron* **2006**, *62*, 6893. (c) Schmidt, A.; Mordhorst, T. *Z. Naturforsch., B* **2006**, *61*, 396. (d) Schmidt, A.; Mordhorst, T.; Nieger, M. *Tetrahedron* **2006**, *62*, 1667. (e) Schmidt, A.; Mordhorst, T. *Synthesis* **2005**, 781. (f) Schmidt, A.; Mordhorst, T.; Habeck, T. *Org. Lett.* **2002**, *4*, 1375.
(21) Roedig, A.; Ibiş, C.; Zaby, G. *Chem. Ber.* **1981**, *114*, 684.
(22) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, **1988**.
(23) Roedig, A.; Zaby, G.; Scharf, W. *Chem. Ber.* **1977**, *110*, 1484.
(24) Roedig, A.; Zaby, G. *Liebigs Ann. Chem.* **1979**, 1614.
(25) Kende, A. S.; Fludzinski, P.; Hill, J. H.; Swenson, W.; Clardy, J. *J. Am. Chem. Soc.* **1984**, *106*, 3551.
(26) Roedig, A.; Bonse, G.; Helm, R.; Kohlhaupt, R. *Chem. Ber.* **1971**, *104*, 3378.
(27) (a) Roedig, A.; Kohlhaupt, R.; Märkl, G. *Chem. Ber.* **1966**, *99*, 698. (b) Roedig, A.; Bauer, H. H.; Heinrich, B.; Kubin, D. *Chem. Ber.* **1971**, *104*, 3525. (c) Roedig, A.; Försch, M.; Geiger, G.; Zaby, G. *Justus Liebigs Ann. Chem.* **1977**, 1267.
(28) Ibiş, C. *Liebigs Ann. Chem.* **1987**, 1009.
(29) Diamond Alkali US 3021370, **1958**; *Chem. Abstr.* **1958**, *57*, 3293.
(30) (a) Smith, A. K.; Streitwieser, A. Jr. *J. Org. Chem.* **1983**, *48*, 2629. (b) Smith, A. K.; Waterman, K. C.; Streitwieser, A. Jr. *J. Org. Chem.* **1985**, *50*, 3360. (c) Waterman, K. C.; Streitwieser, A. Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3874. (d) Feng, A. S.; Speer, D. V.; DiMagno, S. G.; Konings, M. S.; Streitwieser, A. *J. Org. Chem.* **1992**, *57*, 2902.
(31) (a) Weiss, R.; Pomrehn, B.; Hampel, F.; Bauer, W. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1319; *Angew. Chem.* **1995**, *107*, 1446. (b) Weiss, R.; Pühlhofer, F.; Jux, N.; Merz, K. *Angew. Chem. Int. Ed.* **2002**, *41*, 3815; *Angew. Chem.* **2002**, *114*, 3969. (c) Weiss, R.; Bess, M.; Huber, S. M.; Heinemann, F. W. *J. Am. Chem. Soc.* **2008**, *130*, 4610.
(32) Sheldrick, G. M. *SHELXS-97, SHELXL-97: A Program Package for Crystal Structure Solution and Refinement*; University of Göttingen: Göttingen, **1997**.