# An Unorthodox Pathway to the 1,2-Dithiin System<sup> $\star$ </sup>

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Tetracyanoethylene combines with two molecules of thiobenzophenone in refluxing benzene to give the tetrasubstituted 1,2-dithiin 8 (21–29%) besides the corresponding thiophene derivative 9 (40–52%). The X-ray analysis of the ruby-red 8 reveals a half-chair conformation with a torsion angle of 58.9° at the disulfide bond. The thermal desulfuriza-

### Introduction

Highly colored matters aroused the attention of chemists early – and they still do. In 1964/65 the groups of Sörensen<sup>[2]</sup> and Bohlmann<sup>[3]</sup> encountered a deep-red pigment  $C_{13}H_8S_2$  and related compounds in the family of *Asteraceae*. Even after the 1,2-dithiin structure 1 was recognized, the light absorption in the visible was an enigma; it conflicted with the "chemical intuition" for a cyclic conjugated disulfide. No wonder that the open-chain (*Z*)-ethylenedithione structure **2** was suspected of playing a role.

$$R \xrightarrow{S-S} R^{i} \qquad R \xrightarrow{S} R^{i} \qquad R \xrightarrow{S} R^{i} \qquad R \xrightarrow{S} R^{i}$$

$$1 \qquad 2 \qquad 3$$

$$R = CH_{3}-C \equiv C - , \quad R^{i} = -C \equiv C - C \equiv C - CH = CH_{3}$$

The substances – about 10 today – showed antibiotic activity and were named thiarubrines<sup>[4]</sup>. Elegant syntheses of thiarubrine A (1) and B were published recently<sup>[5,6]</sup>; the strategy has still a feature in common with the first access to the parent 1,2-dithiin by Schroth et al.<sup>[7]</sup> in 1965, namely terminal nucleophilic additions to diacetylene and its derivatives.

In a facile thermal or photochemical sulfur loss, 1,2-dithiins are converted to thiophenes, e.g.,  $3^{[3,7b]}$ . This facility vanishes when the dithiin system is fused to further rings; the sulfur extrusion from annellated dithiins requires drastic conditions<sup>[8]</sup>.

Our own pathway to a dithiin was not planned, but has been serendipitous<sup>[9]</sup>. Aromatic thioketones behave Janusfaced in [4 + 2] cycloadditions: they accept 1,3-dienes at the C=S bond<sup>[10,11]</sup>, whereas their formal C=C-C=S system combines with acetylenic<sup>[12,13]</sup> and olefinic dienophiles<sup>[14,15]</sup>. Both functionalities cooperate in the dimerization of thiotion  $\mathbf{8} \to \mathbf{9}$  (benzonitrile, 100°C) proceeds with  $t_{1/2} = 26.7$  h, whereas the sulfur loss induced by triethyl phosphite is a billion times faster. The mechanisms of the formation of  $\mathbf{8}$  and its sulfur extrusion are discussed in the light of recent literature.

fluorenone<sup>[16]</sup>. [2 + 2] cycloadditions can be found in the spontaneous or acid-catalyzed dimerizations of aliphatic or alicyclic thiones which give rise to 1,3-dithietanes<sup>[17]</sup>.

According to Machiguchi et al.<sup>[18]</sup>, tropothione (4) reacts with tetracyanoethylene (TCNE) at 0°C to afford the red heptafulvene-8,8-dicarbonitrile (6, 24%). The assumption of an initial [2 + 2] cycloaddition providing **5** appears well-founded. In the reactions with other dienophiles, tropothione prefers the  $[\pi 8_s + \pi 2_s]$  route closing 5-membered rings<sup>[19]</sup>. TCNE harbors a C=C bond which belongs to the most electron-depleted. TCNE has been the source of delightful new reactions<sup>[20]</sup>.



#### Tetracyanoethylene and Thiobenzophenone

TCNE and 2.1 equiv. of thiobenzophenone (7) were refluxed in benzene for 3 h. Dilution with CCl<sub>4</sub> led to precipitation of the sparingly soluble thiophene derivative 9 (40%). The soluble product – after column chromatography – provided 24% of the 1,2-dithiin 8 in ruby-red prisms. They melt at 212–214°C with elimination of sulfur, resolidify, and melt again at around 290–300°C (impure 9); the pure 9 has a mp of 304–305°C. Although 8 and 9 are 2:1 products, the yields were little dependent on the reactant ratio. Yields of 29% of 8 and 52% of 9 were achieved when 1.7 equiv. of 7 were slowly introduced into the refluxing solution of TCNE in benzene. Chloroform or dichloromethane were likewise suitable as solvents.



On treatment with 2,4-dinitrophenylhydrazine, both 8 and 9 furnished benzophenone 2,4-dinitrophenylhydrazone in high yield, thus confirming the imine character. Middleton, Engelhardt, and Fisher<sup>[21]</sup> obtained 2,5-diaminothiophene (10) from TCNE and hydrogen sulfide at 0°C. We converted 10 into the yellow bis(imine) 9 by reaction with thiobenzophenone in DMF.



In the MS (EI, 70 eV) of dithiin 8 the molecular peak appeared with 16%, and  $M^{+*} - S(9^{+*})$  was the parent peak. Smaller fragments were those likewise observed in the MS of 9. The MS of 8 at 20 eV showed a remarkable difference:  $m/z = 64 (S_2^{+*})$  occurred as the base peak, and  $M^{+*} - 2 S$  was a minor peak (4%); besides  $M^{+*} (23\%)$  and  $M^{+*} - S (26\%)$ , further new signals appeared, among them m/z = 192 (97%).

Our X-ray analysis of 8, carried out in 1987, was probably the first of a 1,2-dithiin derivative; recently, X-ray analyses of the 3,6-disubstituted 1,2-dithiins 13 and 14 by Schroth et al.<sup>[22]</sup> as well as those of four di-annellated 1,2dithiins<sup>[8,23]</sup> have been reported. A glimpse at the ORTEP plot in Figure 1 reveals the half-chair conformation of the heteroring, effectively ruling out a dithione formula 2. The torsional angle at the S-S bond, 58.9°, is that of a normal cyclic disulfide (Table 1). It is virtually identical with the dihedral angle found for the saturated 1,2-dithiane-3,6-dicarboxylic acid  $(60.0^{\circ})^{[24]}$ . The S-S torsional angles of 13  $(54.6^{\circ})$  and 14  $(52.6^{\circ})$  are a little smaller<sup>[22]</sup>, and the four di-annellated dithiins show values from 47° to 60.7°. The recently published microwave structure of 1,2-dithiin (11), the parent, records 53.9° for the C-S-S-C dihedral angle<sup>[25]</sup>.

Figure 1. X-ray crystal structure of 1,2-dithiin **8**, ORTEP plot; thermal ellipsoids represent a 25% probability level



Due to lattice forces, **8** is *chiral* in the crystal. The torsion angles at C6–S1 and at C3–S2 are  $49.4^{\circ}$  and  $36.5^{\circ}$ , respec-

Table 1. Selected bond lengths and angles of the 1,2-dithiin 8 (standard deviation of last significant digit)

Bond lengths [Å]		-	
S1-S2	2.065(2)	C6-S1	1.778(4)
S2-C3	1.766(4)	C3-N2	1.399(5)
C3-C4	1.365(5)	C6-N1	1.396(5)
C4-C5	1.473(5)	$N1=C_{d}$	1.287(5)
C5-C6	1.356(5)	C=N	1.134(5)
Bond angles [°]			
S1-S2-C3	98.6(1)	C5-C6-S1	117.9(3)
S2-C3-C4	119.1(3)	C6-S1-S2	97.2(1)
C4-C4-C5	124.5(3)	N1-C6-S1	124.0(4)
C4-C5-C6	124.2(4)	C6-N1-C <sub>d</sub>	121.2(4)
Torsion angles in h	eteroring [°]		
C6-S1-S2-C3	58.9	C3-C4-C5-C6	35.0
S1-S2-C3-C4	-36.5	C4-C5-C6-S1	5.3
S2-C3-C4-C5	-10.3	C5-C6-S1-S2	-49.4

tively, instead of being identical (Table 1). The differences of several corresponding bond angles and distances likewise go beyond the standard deviations. The imine side chains are attached to the heteroring with different dihedral angles, 149.3° for C4-C3-N2-C<sub>d</sub> and 114.3° for C5-C6-N1-C<sub>d</sub>; we conclude that the conjugation energy of C=C-N=C is not high. The phenyl pairs deviate from coplanarity by 82.5° and 68.2°, respectively.

As expected, the rigid ethylenic systems of the heterocycle contribute little to accommodate the large dihedral angle of the disulfide bond; the torsion angles at C3–C4 and C5–C6 amount to  $10.3^{\circ}$  and  $5.3^{\circ}$ , whereas C4–C5 is twisted by 35°. Accordingly, the bond lengths show the alternation of double and single bonds. The S–S bond length (2.065 Å) fulfils Bock's relation with the torsion angle<sup>[26]</sup> tolerably well. S–S bond lengths of 2.053-2.066 Å were reported for the dithins mentioned above<sup>[8,22,23]</sup>.

The time-averaging <sup>13</sup>C-NMR spectrum of **8** reveals the plane of symmetry. No absorption at  $\delta > 200$  for C=S was observed in the <sup>13</sup>C-NMR spectrum of **8**, in accordance with data on 3,6-disubstituted dithins from Schroth's laboratory<sup>[22,27]</sup>. However, it is an open question whether a 1% equilibrium concentration of a (Z)-dithione of type **2** can be found, since <sup>13</sup>C=S is not a high-intensity signal. The C-3/C-6 signal of **8** appears at  $\delta = 156.7$  and the C-4/C-5 signal at  $\delta = 101.0$ , in agreement with  $C_s$  symmetry. Estimates on the basis of  $\delta_{\rm C}(1,3$ -cyclohexadiene) plus substituent increments<sup>[28]</sup> lead to  $\delta = 157$  and 109, respectively.

The bond system of the 1,2-dithiin escapes the antiaromaticity of a planar 8- $\pi$  system by assuming the half-chair conformation, thereby reducing the repulsion of the lonepair orbitals at the disulfide linkage, too. The conversion of dithiins to thiophenes appears to require an electrocyclic ring-opening furnishing a *cis*-dithione of type **2** as an initiating step. In terms of bond energy, neglecting conjugation, the reorganization consists of  $\pi(CC) + \sigma(SS) \rightarrow 2 \pi(CS)$ . Using bond energies of ethylene, thioformaldehyde, and dimethyl disulfide<sup>[29]</sup>, the net balance would be +33 kcal mol<sup>-1</sup> for the ring-opening. In recent years, ab initio quantum chemical calculations by Mann and Fabian<sup>[30]</sup> have well predicted the structure of 1,2-dithiin (11, S–S 2.082 Å, torsion angle 55.1° by MP2/6-311G\*). The ring-opened *cis*-dithione has become merely a TS on the hypersurface (vide infra), 24 kcal above the ground state of  $11^{[31]}$ .

The red color of 1,2-dithiins remains a tough problem. The calculations mentioned do not permit a participation of the (Z)-dithione, nor do they leave room for a no-bond resonance of the kind discussed for 5,6,6a-trithiapenta-lene<sup>[32]</sup>. Some values of  $\lambda_{max}$  (log  $\varepsilon$ ) for the long-wave absorption of 1,2-dithiins are listed: **11**: 464 nm (3.72)<sup>[22]</sup>; **1**: 488 nm (3.47)<sup>[3]</sup>; **12**: 468 nm (3.51); **14**: 423 nm (2.53)<sup>[22]</sup>. Dithiin **8** shows the strongest bathochromic shift: 509 nm (3.75) in dichloromethane. Concerning the excited states of **11**, calculations by Fabian et al.<sup>[33]</sup> are promising, but not yet convincing.

### TCNE and Thiobenzophenone: The Mechanism

We conjecture a [2 + 2] cycloaddition of the C=S bond of thiobenzophenone (7) to the nitrile group of TCNE as the initial reaction. The process, probably in two steps, furnishes the 2*H*-1,3-thiazete **15**, followed by an electrocyclic ring-opening to give *N*-thioacylimine **16**.



Only a *photochemical* precedent is known to us. As observed by de Mayo et al.<sup>[34]</sup>, irradiation (254 nm) of 7 in acetonitrile afforded the labile *N*-thioacetylimine **18** (33%), and the 2*H*-1,3-thiazete **17** was supposed to be an intermediate. Thiocamphor and related thiones were amenable to the same photocycloaddition with acetonitrile.

Cycloadditions to the C=C bond of TCNE are known, their name is legion<sup>[20b]</sup>. Examples with the C=N bond serving as cycloaddition partner are rare. Several 1,3-dipolar cycloadditions to the nitrile group of TCNE were reported, those of azomethine imine  $19^{[35]}$ , benzonitrile Noxide, and benzonitrile N-sulfide<sup>[36a]</sup>. A pertinent model for our reaction is offered by the 2H-1,3-thiazete 20 which Burger et al. obtained by thermal [4 + 2] cycloreversion of a 1,3,5-oxathiazine precursor<sup>[37]</sup>. The open-chain Nthioacylimine 21 seems to occur in a thermal equilibrium with 20. The analogy with the mobile and solvent-dependent equilibrium of the 1,2-dithiete 23 with dithione 24, studied by de Mayo et al.<sup>[38]</sup>, is obvious. The valence-tautomeric 21 belongs to those reagents which preferentially attack the C=N bond of TCNE; the [4 + 2] cycloadduct 22 (60%) was prepared from 20 and TCNE in refluxing xylene<sup>[39]</sup>.



Our first experiments with 7 and TCNE were carried out in 1:1 molar ratio, and the combined yield of the 2:1 products 8 and 9 exceeded 50%. Thus, the initial 1:1 product 16 must react faster with thione 7 than TCNE itself. The *trans*located nitrile group of 16 appears a priori most likely for the second [2 + 2] cycloaddition giving rise to the 2:1 product 25. The additions of TCNE to benzonitrile *N*-oxide<sup>[36a]</sup> and to heterodiene  $21^{[39]}$  – both run in 1:1 molar ratio – likewise yielded some bisadducts which were conjectured to be derivatives of fumaronitrile.



The formation of **8** by electrocyclization requires the maleonitrile derivative **26**. In our preliminary account<sup>[9]</sup>, we were puzzled by the fact that the *cis-vic*-nitrile group of **16** enters into the second addition of **7**. In the meantime we learned that *mild nucleophilic catalysis* is sufficient for equilibrating tetra-acceptor-substituted ethylenes, e.g., the *trans,cis* pair **27** and **28**<sup>[40]</sup>; even potassium fluoride, dispersed in CDCl<sub>3</sub>, establishes the 88:12 equilibrium. During the reaction of **7** with TCNE, many nucleophilic functions, preferentially the thione sulfur, could act as a catalyst by reversible addition to the C=C double bond of **25** and mediate the *trans,cis* interconversion.

In our experiments, the yield of the thiophene 9 invariably exceeded that of the dithiin 8, although the thermal desulfurization  $8 \rightarrow 9$  is slow; 8 and 9 may well be products of competing reactions. The dithione 26 is an attractive candidate for a common precursor.

#### Conversion of 1,2-Dithiin 8 to Thiophene 9

The smooth formation of thiophenes from dithiins, thermally or light-induced, was noticed early<sup>[3,7]</sup>. The photochemical sulfur extrusion from **12** reaches a quantum yield of 0.7 with visible light<sup>[22]</sup>. Formally, a sulfur atom is ex-

truded; in the *thermal* reaction the occurrence of a singlet sulfur atom ( $\Delta H_{\rm f}^{\rm o} = 93 \text{ kcal mol}^{-1}$ ) is prohibitive.

The thermal sulfur elimination,  $8 \rightarrow 9$ , took place in benzonitrile at 100°C with exclusion of light. In samples withdrawn, the disappearance of the red 8 was measured by spectrophotometry at 550 nm; at this wavelength, the extinction of the yellow 9 was negligible. The slow reaction - 85% conversion after 79 h - was of first order with  $k_1 =$  $7.2 \cdot 10^{-6} \text{ s}^{-1}$ , corresponding to  $\Delta G_{373} = 30.8 \text{ kcal mol}^{-1}$ . However, there was an *induction period* of 6.6 h, determined from the intercept of the linear function of ln  $(E_0/E_t)$  versus time. We ascribe this phenomenon to the slow build-up of a sufficient concentration of a sulfur acceptor.

Recently, Schroth et al. reported some rate constants for thermal desulfurization in DMSO; dithiin 12 lost sulfur 20 times faster than 8 and was exceeded by 14 with another factor of  $5^{[22]}$ .

Dithiin 8 was rapidly desulfurized by *triethyl phosphite* or *triphenylphosphane* at room temp.; here likewise the extinction at 550 nm allowed the kinetic measurement of  $8 \rightarrow 9$  in dichloromethane. In the two runs, illustrated in Figure 2, a 20-fold excess of triethyl phosphite was applied. The pseudo-first order law was obeyed and the average  $k_2 = 0.34 \text{ m}^{-1} \text{ s}^{-1}$  at 23°C was evaluated. This is a 10<sup>9</sup>-fold acceleration of the self-decomposition rate; with the assumption of  $\Delta S^{\pm} = 8 \text{ eu}^{[41]}$ , extrapolation to 23°C furnishes  $k_1 = 3.3 \text{ 10}^{-10} \text{ s}^{-1}$  for the thermolysis rate. Triphenylphosphane ( $k_2 = 0.024 \text{ M}^{-1} \text{ s}^{-1}$ , CH<sub>2</sub>Cl<sub>2</sub>, 23°C) ranks in desulfurization rate behind triethyl phosphite by a factor of 14.

Figure 2. Kinetics of desulfurization of 1,2-dithiin by triethyl phosphite



The *electrocyclic ring-opening* of the 1,2-dithiin is an appealing first step for the desulfurization. Orbital control favors *disrotation* for the ground state and *conrotation* for the first excited state. The half-chair conformation of the 1,2-dithiin can be perceived as the beginning of the conrotatory process which converts the 3,6-disubstituted dithiin to dithione **30**. The TS of disrotation yielding the conformer **29** looks less favorable.

The mentioned ab initio calculations by Mann and Fabian<sup>[30]</sup> disclosed that the TS of disrotatory ring-opening of 11 is located at  $\Delta H = +24.2$  kcal mol<sup>-1</sup> above the ground state (CASSCF (12,8)/3-21G\*); its structure is close to a somewhat twisted 29 (R = H) which likewise does not con-



stitute a minimum on the hypersurface. In contrast, conformation **30** (R = H) is an intermediate at  $\Delta H$  = +18.4 kcal mol<sup>-1</sup> above the ground state of **11**; with +15 kcal mol<sup>-1</sup> the *s*-*trans*,*Z*,*s*-*trans* form **31** (R = H) is more favorable<sup>[31]</sup>. The authors also calculated 3,6-diamino-1,2-dithiin-4,5-dicarbonitrile which is more closely related to **8**; the conformation corresponding to **31** is *below* the dithiin level by 1.0 kcal mol<sup>-1</sup>.

Deeper mechanistic insight has recently been achieved for the *photochemical* sulfur extrusion. In an elegant experiment, Block et al. irradiated the 1,2-dithiins 1, 11, and 12 with visible light at  $-70^{\circ}$ C; the bicyclic thiiranes 32 were generated and characterized by their spectra<sup>[42]</sup>. Thiophenes are formed on further exposure to light. The conrotatory ring-opening furnished 30 which was converted to 32 by an intramolecular cycloaddition. When the irradiation of 11 was repeated in the matrix at 25 K, the reaction came to a halt at the *s-cis,Z,s-trans*-butenedithial (30, R = H).

The conversion  $30 \rightarrow 32$  offers a new example of a general principle which was recognized by George, Mitra, and Sukumaran in 1980<sup>[43]</sup>. Besides the disrotatory electrocyclization giving cyclohexadienes, 1,3,5-hexatrienes can undergo a *photochemical* [ $\pi 4_a + \pi 2_s$ ] cycloaddition. Many hetero-1,3,5-hexatrienes are amenable to this kind of photocyclization. Closely related to the sequence  $11 \rightarrow 30 \rightarrow 32$  is the two-photon process converting isothiochromene 33 to the indene 1,2-episulfide 34; isolated was the product of photochemical sulfur extrusion by Padwa et al.<sup>[44]</sup>.

For the *thermal reactions* of hetero-1,3,5-hexatrienes, there exists an alternative to the 1,6-cyclization, too: a 1,5electrocyclization giving rise to zwitterions<sup>[43]</sup>. The exothermic formation of furoxane 36 from the 1,2-dinitrosoethylene derivative 35<sup>[45]</sup> may serve as an example. The corresponding process  $26 \rightarrow 37$  can simply be described as an intramolecular nucleophilic addition. The Indian authors stated that the  $[\pi 4_a + \pi 2_s]$  cycloadduct has not been observed in a thermal reaction of a hetero-1,3,5-hexatriene<sup>[43]</sup>. Due to the weakness of the  $\pi$  bond in C=S, a conversion of 37 into the thiirane 38 appears thermodynamically probable here. According to PM3 calculations of the molecule with 4H instead of 4  $C_6H_5$ , the energy level of 38 is below that of 37 by 15 kcal  $mol^{-1}$ , and the advantage of 38 grows to 27 kcal mol<sup>-1</sup> with Becke3LYP/6-31G\* + ZPVE<sup>[46]</sup>. Zwitterion 37 is not even a minimum on the energy surface in the ab initio calculations.

Thus, thiirane **38** is the most likely candidate for the sulfur extrusion reaction which terminates the sequence of re-



versible steps and profits from the aromaticity of thiophene 9. The thermal loss of sulfur from thiiranes like 38 concerns a much documented<sup>[47]</sup>, but mechanistically still enigmatic process. The occurrence of the sulfur atom, a thermochemical obstacle, is circumvented by *concatenation*: the sulfur chain is built up on a supporting molecule; when long enough, the chain will roll up and shed cyclooctasulfur or other cyclic species  $S_x^{[48]}$ . Transfer of formal sulfur atoms between anionic sulfur chains is very fast. It was observed in our laboratory that sodium thiophenoxide is a highly active catalyst in the desulfurization of phenylated thiiranes; a stepwise growth of the sulfur chain was assumed<sup>[49]</sup>. In our case here, a constituent of the reaction medium might temporarily offer "shelter" for the sulfur of 38, e.g., the thione groups of 26 could desulfurize thiirane 38. We demonstrated the smooth desulfurization of phenylated thiiranes by aliphatic and aromatic thioketones<sup>[50]</sup> furnishing thione S-sulfides 39; we proposed a concatenation pathway for the rapid conversion of **39** to thiones + S<sub>8</sub>; the same explanation was given for the decomposition of aromatic nitrile N-sulfides by Howe et al.<sup>[36b]</sup>.



P<sup>III</sup> compounds are nucleophilic-electrophilic reagents; their capability of back-donation generates  $\sigma + \pi$  bond in two-center processes<sup>[51]</sup>. Phosphanes and phosphites are standard reagents for the conversions of thiiranes to olefins. Structure **40** may be proposed as an intermediate which suffers cheletropic elimination of R<sub>3</sub>PS. The second-order rate for the desulfurization  $\mathbf{8} \rightarrow \mathbf{9}$  with PR<sub>3</sub> would be compatible with either capturing **38** at the end of an equilibrium sequence or with a *direct attack* on 1,2-dithiin **8**. The billionfold rate enhancement by triethyl phosphite clearly speaks for the second pathway, a nucleophilic substitution at the S-S bond of **8** giving rise to **41**. Another nucleophilic substitution, now by the thiolate function, closes the thiophene ring affording **9**.

### Further Thiophenes from Thiones and TCNE

Not much effort was spent to extend the reaction with TCNE to other thiones. 4,4'-Dimethoxythiobenzophenone and TCNE were refluxed in chloroform and furnished 78% of thiophene 43, whereas xanthione and thioxanthione did not interact with TCNE under these conditions. The reaction of 2,4-dichlorothiobenzophenone (42) in boiling chlorobenzene provided 44 (25%). No 1,2-dithiins were isolated. The new thiophenes have a higher solubility than 9 and permit better NMR data.



The C-3/C-4 signal of 43 at  $\delta_{\rm C} = 103.9$  reveals the highfield shift by the cyano groups, compared with  $\delta_{\rm C} = 126.4$ for the parent thiophene. The  $\delta$  value of 156.6 (124.9 for thiophene itself) for C-2/C-5 results from the deshielding effect of the imino function. The imino C atom signal of 43 at  $\delta = 168.7$  does not differ much from the signal of 1,2dithiin 8 ( $\delta = 172.7$ ).

The <sup>1</sup>H-NMR spectrum of **43** at  $-20^{\circ}$ C (CDCl<sub>3</sub>, 80 MHz) reveals two different methoxyphenyl groups; they are in coalescence at  $+34^{\circ}$ C, and at 100°C the signal of the averaged methoxyphenyl groups has sharpened again. The dynamic process is probably the N inversion at the imine functions<sup>[52]</sup>. The <sup>13</sup>C-NMR spectrum at  $+32^{\circ}$ C (20 MHz) displays "recovery" after the coalescence phase; there is *one* set of signals for C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>, but some of the singlets in the H-decoupled spectrum are still broad.



In the MS of the thiophenes 9, 43, 44, the molecular peaks are the most populous despite m/z up to 634. With four Cl atoms and a sulfur function besides <sup>13</sup>C, the MS of 44 is an orgy of isotope peaks; the disentanglement clarified the molecular formulae of the fragments. Peaks of modest strength result from the breaking away of one side-chain: the ions with loss of N=CAr<sub>2</sub> occur with 2–6% in the three spectra. The counterpart appears in the MS of 44; the structure 45 (22%) of a nitrilium ion (Beckmann-type rearrangement) is likely. Major fragments of 9<sup>+•</sup> are the benzhydryl cation (17%) and the fluorenyl cation (47, 46%). In the MS of 44, the monochlorofluorenyl (50, 36%) exceeds the population of the dichlorofluorenyl cation (49, 8%), and a peak

at m/z = 165 even points to fluorenyl (47, 21%). Among many specific fragments, m/z = 211 (20%) in the MS of 43 may be mentioned; the quinomethane derivative 46 is conceivable.

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## **Experimental Section**

Instruments and Methods<sup>[53]</sup>: Chromatography on silica gel: CC: column; PLC: preparative thick layer (2 mm); TLC: thin layer. Intensities of isotope peaks in the MS are given in the form, e.g., <sup>13</sup>C calcd./found.

3,6-Bis[(diphenylmethylene)amino]-1,2-dithiin-4,5-dicarbonitrile (8). - a) Thiobenzophenone (7, 3.60 g, 18.2 mmol, 2.12 equiv.) and 1.10 g (8.6 mmol) of tetracyanoethylene (TCNE) were refluxed in 15 ml of dry benzene for 3 h under argon and with exclusion of light; the reaction can be monitored by TLC (CH<sub>2</sub>Cl<sub>2</sub>). After cooling, 50 ml of CCl<sub>4</sub> was added; a yellow-brown solid was filtered and washed with CCl<sub>4</sub>: 1.70 g (40%) of crude 9 was obtained. The solvent was removed from the mother liquor; after CC (CH<sub>2</sub>Cl<sub>2</sub>) and recrystallization from THF/pentane (1:1), the dark-red residue gave 1.10 g (24%) of 8 in ruby-red crystals; the purification by CC is mandatory for obtaining an analytically pure specimen. On slow heating, the specimen sinters and loses some color above 190°C, forms a viscous brown melt at 212-214°C, resolidifies and melts above 290°C; some S<sub>8</sub> sublimes in the mp tube. – IR (KBr);  $\tilde{v}$  = 693, 700 cm<sup>-1</sup> st, 766, 789 m (C<sub>6</sub>H<sub>5</sub> wagg.); 992, 1146 m, 1321 st; 1447 m, 1556 br. st, 1607 st (arom. C=C and C=N), 2216 m (C=N). – UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log  $\epsilon$ ) = 509 nm (3.75), 376 (4.23), 270 (4.46).  $- {}^{1}H$  NMR (CDCl<sub>3</sub>):  $\delta = 7.48$  (br. s, 4 C<sub>6</sub>H<sub>5</sub>). - <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 101.0 (s, C-4/C-5), 114.5 (s, 2 CN); 128.7, 129.7, 132.2 (3 d, 20 arom. CH), 136.6 (s, 4 arom. C<sub>a</sub>), 156.7 (s, C-3/C-6), 172.7 (s, 2 C=N). - MS (70 eV, 160°C); m/z (%): 524 (16)  $[M^+; {}^{13}C 5.6/6.1; {}^{34}S + {}^{13}C_2 2.4/2.4], 492 (100) [M^+ - S; {}^{13}C$ 36/39], further fragments as described for the MS of 9. (20 eV, 160°C) m/z (%): 524 (23) [M<sup>+</sup>; <sup>13</sup>C 8.2/7.4; <sup>34</sup>S + <sup>13</sup>C<sub>2</sub> 3.5/3.9], 492 (26)  $[M^+ - S]$ , 465 (18)  $[492 - HCN; {}^{13}C 6.3/8.4]$ , 460 (4)  $[M^+ -$ 2 S], 459 (3.7) [M<sup>+</sup> - HS - S], 256 (60), 224 (42) [C<sub>14</sub>H<sub>10</sub>NS<sup>+</sup>?], 192 (97)  $[C_{14}H_{10}N^+?]$ , 160 (72), 128 (47), 126 (35), 121 (8), 64 (100)  $[S_2^+]$ . -  $C_{32}H_{20}N_4S_2$  (524.6): calcd. C 73.25, H 3.84, N 10.68, S 12.22; found C 73.25, H 3.91, N 10.71, S 12.27. - Mol. mass. 510 (vapor phase osmometry, benzene,  $37^{\circ}$ C). – b) 3.12 g (15.7 mmol, 1.73 equiv.) of 7 in 15 ml of dry benzene was added dropwise to 1.16 g (9.06 mmol) of TCNE in 10 ml of refluxing benzene within 3 h (exclusion of light). After further refluxing for 3 h and dilution with 70 ml of CCl<sub>4</sub>, work-up as above afforded 2.00 g (52%) of crude 9 and 1.18 g (29%) of recrystallized 8. - c) 21.2 mmol of 7 (1.3 equiv.) and 16.4 mmol of TCNE were refluxed in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> and 10 ml of CHCl<sub>3</sub> for 20 h. Precipitation with 50 ml of CCl<sub>4</sub> yielded 2.65 g of crude 9; after removal of excess TCNE by sublimation, 2.35 g (45%) resulted. On concentration of the mother liquor, 1.30 g (23%) of 8 crystallized. -d) 10.0 mmol of 7 reacted with 6.3 mmol of TCNE in 150 ml of boiling CHCl<sub>3</sub>, i.e., in more dilute solution, for 20 h. Addition of 150 ml of CCl<sub>4</sub> and cooling to  $-20^{\circ}$ C gave 1.10 g of crude **9** and, after recrystallization from pyridine, 804 mg (33%) of pure **9**; 550 mg (21%) of **8** were isolated from the CCl<sub>4</sub> mother liquor.

X-ray Analysis of 1,2-Dithiin 8: A single crystal of 8 was sealed in a glass capillary and mounted on the goniometer head of a Siemens R3m four-circle diffractometer operating with Mo- $K_{\alpha}$  radiation and a graphite monochromator. The unit cell dimensions resulted from a least-squares fit of the setting angles of 20 centered strong reflections, followed by a check of axial and Laue symmetry. ω-scans with intensity-dependent variable scan speed and 1.2° scan range were used to scan the reflections in a quadrant. Lorentz and polarisation correction of the data led finally to 3982 unique reflections with  $I > 4\sigma(I)$ . The structure was solved by direct methods implemented in the SHELX programs (Siemens Analytical Instruments, version 2.1). Non-hydrogen atoms were refined anisotropically with inclusion of hydrogen atoms in calculated positions and fixed isotropic U using the SHELXTL 93 programs (G. W. Sheldrick, University of Göttingen, 1993). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100147. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@chemcrys.cam.ac.uk].

Table 2. Crystal data and data collection parameters

Compound		
Chem. formula	C32 H20 N4 S2	
Form. wght.	524.64	
Cryst. size [mm]	0.3x0.3x0.5	
Cryst. system	Monoclinic	
Space group	P2(1)/n	
a, [Å]	11.611(2)	
b, [Å]	16.884(3)	
c, [A]	13.970(3)	
α, [°]	90.00	
β, [°]	90.60(3)	
γ, [°]	90.00	
V, [Å <sup>3</sup> ]	2738.5(9)	
Ζ	4	
p(calcd.), [Mg/m3]	1.272	
μ [mm <sup>-1</sup> ]	0.222	
F(000)	1088	
Index range	0 ≤h≤13 0 ≤k≤19	
	<b>-15</b> ≤l≤15	
2 0 [°]	48.00	
Temp, [K]	293(2)	
Refl. collected	4186	
Refl. unique	3982	
Refl. observed (4o)	2634	
R (int.)	0.0272	
No. variables	334	
Weighting scheme <sup>1</sup>	0.0533/2.9849	
x/y		
GOOF	1.059	
Final R (4o)	0.0622	
Final wR2	0.1323	
Larg. res. peak	0.216	

$${}^{1}w^{-1} = \sigma^{2}F_{0}^{2} + (xP)^{2} + yP; P = (F_{0}^{2} + 2F_{c}^{2})/3.$$

2,5-Bis[(diphenylmethylene)amino]thiophene-3,4-dicarbonitrile (9): The orange-yellow crystals (pyridine) melted at  $304-305^{\circ}$ C without decomposition. Sublimation at 250°C/0.01 Torr in the Kugelrohr was likewise suitable for purification. – IR (KBr):  $\tilde{v} = 693$  cm<sup>-1</sup>, 704 st, 759, 784 m (C<sub>6</sub>H<sub>5</sub> wagg.); 1298, 1320 st; 1565 st br. (arom. ring vibr., C=N), 2224 (conjug. C≡N). – UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log ε) = 428 nm (4.36), 300 (4.20), 256 (4.47). – <sup>1</sup>H NMR (CDCl<sub>3</sub>, -20°C): a well-resolved m at δ = 7.06–7.81 allows to recognize two different C<sub>6</sub>H<sub>5</sub>; at 30°C the m is close to coalescence. – <sup>13</sup>C NMR ([D<sub>6</sub>]pyridine, 90°C, 25.2 MHz, little resolved due to low solubility); comparison of the H-decoupled spectrum with that of **43** allows tentative assignments: δ = 106 (C-3/C-4 of thiophene), 112 (2 C≡N), 131 (C-2/C-6 of C<sub>6</sub>H<sub>5</sub>), 156 (C-2/C-5 of thiophene), 170 (2 C≡N). – MS (70 eV, 170°C); *m/z* (%): 492 (100) [M<sup>+</sup>], 459 (1.7) [M<sup>+</sup> – SH; <sup>13</sup>C 0.60/0.68], 415 (2.1) [M<sup>+</sup> – C<sub>6</sub>H<sub>5</sub>; <sup>13</sup>C 0.61/ 0.52], 312 (5.8) [M<sup>+</sup> – NC(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>], 310 (4.8), 246 (5.8), 194 (4), 167 (17) [benzhydryl<sup>+</sup>], 165 (46) [fluorenyl<sup>+</sup>, **47**], 121 (5.4), 79 (11), 77 (10) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>]. – C<sub>32</sub>H<sub>20</sub>N<sub>4</sub>S (492.6): calcd. C 78.02, H 4.09, N 11.38, S 6.51; found C 78.33, H 4.05, N 11.15, S 6.13.

Cleavage with 2,4-Dinitrophenylhydrazine (DNPH). – a) 121 mg (0.23 mmol) of **8** and 116 mg (0.58 mmol) of DNPH in 3.5 ml of ethanolic sulfuric acid (5%) were refluxed for 3 h. After cooling, the orange needles of *benzophenone 2,4-dinitrophenylhydrazone* (146 mg, 88%), mp 235–237°C, were filtered; mixed mp with an authentic specimen showed the identity. – b) The reaction of the less soluble **9** (420 mg, 0.85 mmol) with 466 mg (2.35 mmol) of DNPH in 14 ml of ethanolic H<sub>2</sub>SO<sub>4</sub> (5%) required refluxing for 12 h: 608 mg (99%), mp 235–237°C, mixed mp.

Conversion of 8 to 9. -a) 32 mg of 8 in 4 ml of ethanol/CHCl<sub>3</sub> (9:1) was refluxed for 2 d; TLC no longer showed 8. At  $-25^{\circ}C$  25 mg (83%) of 9 crystallized, mp and mixed mp 304 $-306^{\circ}C$ . -b) When 524 mg (1.00 mmol) of 8 and 289 mg (1.10 mmol) of triphenylphosphane in 3 ml of CHCl<sub>3</sub> reacted at room temp. for 4 h, the color changed from red to yellow. On addition of 10 ml of CCl<sub>4</sub>, 438 mg (89%) of 9 crystallized, mp 301 $-305^{\circ}C$ .

Kinetics of Desulfurization of 8: The conversion  $8 \rightarrow 9$  was monitored spectrophotometrically (Perkin-Elmer, Lambda-3) at 550 nm; the extinction coefficients in CH<sub>2</sub>Cl<sub>2</sub> are 4400 for 8 and negligible for 9. The wave-length of 550 nm is beyond  $\lambda_{max}$  (509 nm,  $\varepsilon =$ 5570), but still in the region of moderate slope of the absorption curve. The desulfurization with ca. 20 equiv. of P<sup>III</sup> compounds followd the pseudo-first order. – a) 8 (2.17 mg, 4.14 µmol) was dissolved by shaking with 15 ml of 5.67 mM *triethyl phosphite* (20.5 equiv.) in CH<sub>2</sub>Cl<sub>2</sub>, thermostated at 23°C in a 5-cm quartz cuvette. After some min at 23.0 ± 0.2°C, the zero-time and  $E_o$  (1.06) were defined and the decrease of extinction monitored for 18 min. The residual  $E_{\infty} = 0.057$  after 8 h was ascribed to an impurity of the starting material; this is justified by the optimal fitting of 18  $E_t$ values with the function

$$k_{1\psi}t = \ln \frac{E_o - E_\infty}{E_\ell - E_\infty} \tag{1}$$

 $E_t$  readings up to 86% conversion were subjected to least-square treatment (Figure 2) which gave  $k_{1\psi} = 1.82 \cdot 10^{-3} \text{ s}^{-1}$  with a correlation coefficient r = 0.9999. Division by the phosphite concentration at half-reaction furnished  $k_2 = 0.329 \text{ m}^{-1} \text{ s}^{-1}$ . - b) In a second run, 1.13 µmol of 8 and 25.1 µmol of triethyl phosphite (22.2 equiv.) reacted in 3 ml of CH<sub>2</sub>Cl<sub>2</sub> in a 1-cm cuvette at 23°C. Starting with  $E_0 = 0.910$  at 550 nm, 17  $E_t$  readings showed 95% conversion  $8 \rightarrow 9$  in 17 min; after 8 h,  $E_{\infty} = 0.015$  remained. Linearization provided  $k_{1\psi} = 2.89 \cdot 10^{-3} \text{ s}^{-1}$  and  $k_2 = 0.354 \text{ m}^{-1} \text{ s}^{-1}$ . - c) Analogously, 8 (0.403 mm) was treated with triphenylphosphane (8.07 mm, 20 equiv.) in 3 ml of CH<sub>2</sub>Cl<sub>2</sub> at 23°C in the 1-cm cuvette. Due to disturbances in the initial phase,  $E_0 = 0.785$  was defined after 15 min as zero time, and 22  $E_t$  values from 5-81% conversion in 147 min gave  $k_{1w} = 1.92 \cdot 10^{-4} \text{ s}^{-1}$  with r = 0.9999. Division by 7.9 mm for the mean concentration of  $(C_6H_5)_3P$  furnished  $k_2 = 0.0243 \text{ m}^{-1} \text{ s}^{-1}$ . - d) Self Decomposition of 8: Preliminary experiments in mesitylene at 100°C showed erratic results. Pure benzonitrile, freshly distilled and flushed with argon, was a suitable solvent. **8** (12.30 mg, 23.4 µmol) was dissolved in benzonitrile, preheated to 100°C, in a 100-ml volumetric flask which had been purified with caroic acid. The flask was kept in a thermostat at 100.0  $\pm$  0.5°C in the dark, and 3-ml samples were withdrawn and cooled to 23°C in a 1-cm cuvette; the extinction was recorded at 550 nm. Within 79 h 85% of **8** was converted. The  $E_{\infty}$  reading (0.030) was taken after exposing the flask for some hours to diffuse daylight. The function according to eq. (1) showed an induction period. Nine concentration measurements between 31.4 and 79 h ( $E_t = 0.517 - 0.148$ ) gave  $k_1 = 7.20 \cdot 10^{-6} \text{ s}^{-1}$  on least-square treatment. From the intercept of the straight line (r = 0.9998) an induction period of 6.6 h was evaluated.

Synthesis of 9: 2,5-Diaminothiophene-3,4-dicarbonitrile (10) was prepared from TCNE and  $H_2S$  in 91% yield<sup>[21]</sup>. The colorless 10 (82 mg, 0.50 mmol) and 0.6 g of 7 were refluxed in 6 ml of DMF for 3 h. After removal of the solvent at 20 Torr, the blue residue was refluxed with 3 ml of CHCl<sub>3</sub> and 15 ml of CCl<sub>4</sub>. Filtering after cooling furnished 152 mg (62%) of 9, mp and mixed mp 304–306°C. The low basicity of 10 (insoluble in aqueous acids<sup>[21]</sup>) required drastic conditions for imine formation.

2,5-Bis {[bis(4-methoxyphenyl)methylene]amino}thiophene-3,4dicarbonitrile (43): 4,4'-Dimethoxythiobenzophenone<sup>[54]</sup> (0.905 g, 3.50 mmol) and 0.680 g (5.31 mmol) of TCNE in 40 ml of CHCl<sub>3</sub> were refluxed for 10 h. After cooling to -60°C, 0.72 g of a mixture was filtered and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>: 0.59 g from which excess of TCNE was removed by sublimation at 100°C/20 Torr, and 325 mg of 43 remained. The CH<sub>2</sub>Cl<sub>2</sub> mother liquor was purified by CC (CH<sub>2</sub>Cl<sub>2</sub>) and gave further 516 mg of 43 (together 78%); yellow crystals, mp 227–229°C. – IR (KBr):  $\tilde{v} = 842 \text{ cm}^{-1} \text{ m}$ (C<sub>6</sub>H<sub>4</sub> wagg.); 1149, 1174 st, 1253 vst (C-O); 1502, 1545, 1568 st (arom. ring vibr.), 1600 st (C=N), 2220 m (C=N). - <sup>1</sup>H NMR  $(CDCl_3, -20^{\circ}C, 80 \text{ MHz}): \delta = 3.92, 4.00 (2 \text{ s}, 2 \text{ OCH}_3 \text{ each}), 6.89$ and 7.74 (2 d, AB, J = 9 Hz, 2 C<sub>6</sub>H<sub>4</sub>), 6.96 (s, A<sub>2</sub>, 8H of 2 C<sub>6</sub>H<sub>4</sub>); one signal of AB was superimposed by the s of  $A_2$ ; (CDCl<sub>3</sub>, 34°C):  $\delta = 3.86$  (s, 4 OCH<sub>3</sub>), C<sub>6</sub>H<sub>4</sub> protons in coalescence; ([D<sub>6</sub>]DMSO, 100°C):  $\delta = 3.92$  (s, 4 OCH<sub>3</sub>), 7.03, 7.35 (AA'BB' of 4 C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 32°C, 20.2 MHz):  $\delta = 55.4$  (q, 4 OCH<sub>3</sub>), 103.9 (s, C-3/C-4 of thiophene), 113.0 (s, 2 CN), 114.3 (d, sharp, C-3/C-5 of 4-anisyl), 126.5 (s, br., C-1 of 4-anisyl), 131.2 (d, br., C-2/C-6 of 4-anisyl), 156.6 (s, C-2/C-5 of thiophene), 162.5 (s, br., C-4 of 4anisyl), 168.7 (s, 2 C=N); signals of 3 out of 4 nonequiv. C of panisyl are broadened by exchange. - MS (70 eV, 240°C); m/z (%): 612 (100)  $[M^+, {}^{13}C 40/42; {}^{34}S + {}^{13}C_2 12.3/13.6], 581 (1.2) <math>[M^+ -$ OCH<sub>3</sub>; <sup>13</sup>C 0.50/0.50], 579 (1.6) [M<sup>+</sup> - HS; <sup>13</sup>C 0.65/0.61], 372 (1.6)  $[M^+ - NC(anisyl)_2, C_{21}H_{14}N_3O_2S^+; {}^{13}C 0.37/0.43], 306$  (6), 226 (8) [C<sub>15</sub>H<sub>14</sub>O<sub>2</sub><sup>+</sup>], 225 (4) [**48**], 211 (20) [C<sub>14</sub>H<sub>11</sub>O<sub>2</sub><sup>+</sup>, **46**], 195 (4)  $[C_{14}H_{11}O^+, 225 - CH_2O], 183 (6), 168 (8), 152 (6), 151 (8), 140$ (7), 139 (7), 113 (5), 77 (7).  $-C_{36}H_{28}N_4O_4S$  (612.7): calcd. C 70.57, H 4.61, N 9.15, S 5.23; found C 70.75, H 4.76, N 9.09, S 5.13.

2,5-Bis {[(2,4-dichlorophenyl)(phenyl)methylene ]amino}thiophene-3,4-dicarbonitrile (44): 2,4-Dichlorothiobenzophenone<sup>[54]</sup> (42, 1.23 g, 4.60 mmol) and 860 mg (6.71 mmol) of TCNE in 20 ml of chlorobenzene were refluxed for 4 h. The residue after removal of the solvent was subjected to CC; CCl<sub>4</sub> eluted 200 mg of 42, and with CHCl<sub>3</sub> 720 mg of a mixture followed. After recrystallization from CCl<sub>4</sub>, 367 mg (25%) of the pure yellow 44, mp 298-300°C, was obtained. The analytical sample was sublimed at 250°C/0.01 Torr. – IR (KBr):  $\tilde{v} = 701 \text{ cm}^{-1}$ , 780 (C<sub>6</sub>H<sub>5</sub> wagg.), 821, 1059, 1098 (C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub> wagg.); 1240, 1299, 1319, 1383; 1450, 1461 (arom. ring vibr.), 1569 st br. (C=N), 2232 (conj. C=N). –

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 7.0-7.8$  (structured m, 16 arom. H). -MS (70 eV, 280°C), the expected ratio for isotopes with 0-4 <sup>37</sup>Cl 77.96:100:47.82:10.19:0.82; m/z (%): 628 (70.4) [M<sup>+</sup>, is C<sub>32</sub>H<sub>16</sub><sup>35</sup>Cl<sub>4</sub>N<sub>4</sub><sup>32</sup>S, <sup>13</sup>C 25/26], 630 (100) [M<sup>+</sup> with <sup>35</sup>Cl<sub>3</sub><sup>37</sup>Cl<sup>32</sup>S 90.3 +  ${}^{35}\text{Cl}_{4}{}^{34}\text{S}$  3.1 +  ${}^{13}\text{C}_{2}$  4.4, calcd. 97.8;  ${}^{13}\text{C}$  36/35], 632 (53.4) [M<sup>+</sup> with  ${}^{35}\text{Cl}_2{}^{37}\text{Cl}_2{}^{32}\text{S}$  43.2 +  ${}^{35}\text{Cl}_3{}^{37}\text{Cl}^{34}\text{S}$  4.4 +  ${}^{13}\text{C}_2$  6.2, calcd. 53.8;  $^{13}C$  19/18], 634 (13.3) [M<sup>+</sup> with  $^{35}Cl_3^{37}Cl_3^{32}S$  9.2 +  $^{35}Cl_2^{37}Cl_2^{34}S$  $2.4 + {}^{13}C_2$  3.3, calcd. 14.9;  ${}^{13}C$  4.7/4.2]; the assignment of further fragments were likewise based on isotope peaks, but they are not listed; 593 (13)  $[M^+ - Cl]$ , 380 (2.5)  $[M^+ - 45, C_{19}H_8Cl_2N_3S^+]$ , 345 (12) [380 - Cl, 4, <sup>13</sup>C of 344, 8], 344 (37) [380 - HCl], 248 (22) [C<sub>13</sub>H<sub>8</sub>Cl<sub>2</sub>N<sup>+</sup>, **45**], 233 (7.9) [1,3-dichlorofluorenyl<sup>+</sup>, **49**], 199 (36) [50], 163 (22) [199 - HCl,  $C_{13}H_{17}^+$ ], 165 (21) [47], 146 (7.4)  $[C_6H_4Cl_2^+]$ , 145 (4.7)  $[C_6H_3Cl_2^+]$ , 105 (29)  $[C_7H_7N^+]$ , 77 (25) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>]. - C<sub>32</sub>H<sub>16</sub>Cl<sub>4</sub>N<sub>4</sub>S (630.4): calcd. C 60.97, H 2.56, N 8.89, S 5.09; found C 61.01, H 2.48, N 8.79, S 5.02.

- \* Dedicated to Professor *Wolfgang Beck*, München, on the occasion of his 65th birthday.
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