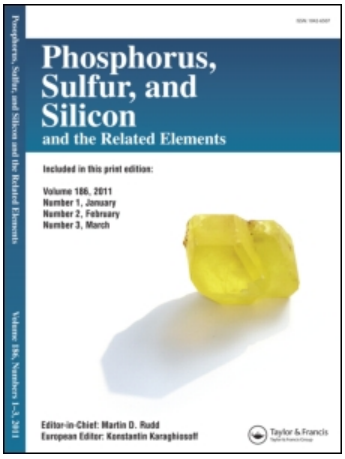

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REACTIONS OF 2-ARYL-2-IMINIO DITHIOACETATES: CONVENIENT SYNTHESES OF SULFUR AND NITROGEN ANALOGUES OF 2-OXO CARBOXYLIC ACIDS

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REACTIONS OF 2-ARYL-2-IMINIO DITHIOACETATES: CONVENIENT SYNTHESES OF SULFUR AND NITROGEN ANALOGUES OF 2-OXO CARBOXYLIC ACIDS

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The new 2-aryl-2-iminio dithioacetates **1** are easily available by reaction of acetophenones with different sulfurdioxide—secondary amine complexes and sulfur. A short summary of the syntheses and reactions of related zwitterionic compounds **2–5** is given. The 2-iminium dithioester salts **6** have been prepared by reaction of **1** with several alkylating agents. The hydrolysis of **6** is a new route to 2-oxo dithioesters **7**. Because the iminium function in **6** is of higher reactivity in reaction with amines than the dithioester group the novel 2-imino dithioesters **10** and 2,2-diamino dithioesters **12** could be synthesized by reaction of **6** with primary and secondary amines, respectively. **5a** was converted into the cyclic monothiooxamide **17** by application of the synthetic strategy to the compounds of the diaminocarbenium dithiocarboxylate type **4** and **5**. X-ray structure determinations of **6a**, **10f** and **12b** are presented as examples of these new classes of dithioesters.

Keywords: dithiocarboxylate; 2-imino-; dithioester; 2-oxo-; 2-imino-; 2,2-diamino-; iminium salt; monothiooxamide; thiolation type reaction

INTRODUCTION

Acetophenones can be easily converted to the 2-aryl-2-iminio-dithioacetates **1** by a new SO_2-assisted thiolation type reaction[1] (Scheme 1).

Although compounds like **2–5** have been known for 30 years, their potential for synthesis of sulfur and nitrogen analogous 2-oxo carboxylic acid derivatives has not been studied. We report here efficient syntheses of heteroanalogous

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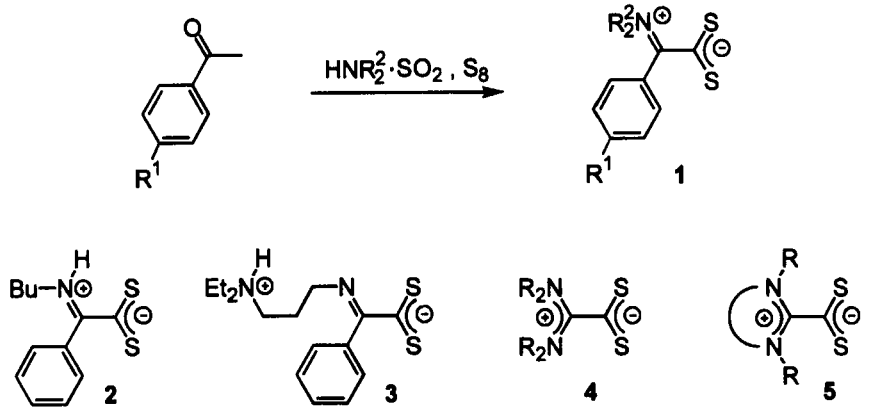


SCHEME 1

2-oxo carboxylic acid derivatives including some novel classes of dithioesters starting from 2-aryl-2-iminio dithioacetates **1**[2].

The two related betaines **2** and **3** were described by Asinger *et al.*, however, the proposed structure of **3** was not unambiguously determined[3]. We were able to show by X-ray crystal structure analysis, including the localization of the N-bonded H-atom, that **3** exists in the ammonium form[4]. The only known reaction of **2** and **3** is the reversible addition of five equivalents of elemental sulfur which in our experience does not result in the formation of 1,2,3,4,5,6-hexathiocan-7-thiones[3,5] but 1,2,3,4,5,6,7-heptathiocanes[6]. The related diaminocarbenium dithiocarboxylates **4** and the analogous heterocyclic compounds **5** can usually be synthesized by reaction of carbon disulfide with tetraamino ethylenes[7–9] or stable diamino carbenes[10] and by thiolation type reactions of enediamines[11] and activated enediamines (2-chloro and 2-phenoxy substituted 1,1-diamino ethylenes)[12] with elemental sulfur. Furthermore, some other miscellaneous syntheses are known[13]. With the exception of cycloadditions[7,8,14], reactions of **2–5** were not investigated systematically. Only S-methylations[7,11,12,15], an S-protonation[11] and the reaction of a 4,5-dihydro-1*H* imidazolium-2-dithiocarboxylate (type **5**) with selenium to give an imidazolidin-2-selenone[16] were described.

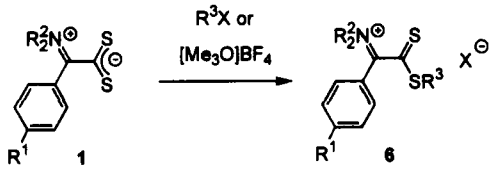
RESULTS AND DISCUSSION

Syntheses

2-Aryl-2-iminio dithioacetates **1a–f** are easily available by reaction of acetophenones with sulfur and secondary amines in the presence of sulfur dioxide, or

even better, directly with sulfur dioxide—secondary amine complexes[1] (Scheme 1). Compounds **1** rapidly undergo alkylation with several alkylating agents such as alkyl iodides, benzyl bromide, dimethyl sulfate or trimethyloxonium tetrafluoroborate in acetonitrile at room temperature (Scheme 2). The [(alkylthio-thiocarbonyl)-methylene] substituted dimethylammonium, pyrrolidinium and piperidinium salts **6** obtained, from now on referred to as (2-iminium substituted) dithioester (salts), served as key components in further synthetic reactions. These salts are stable over years at 4°C in an inert gas atmosphere. **6i** and **k** are intermediates in the synthesis of 2-oxo dithioesters **7** and were not isolated.

All literature methods for the synthesis of 2-oxo dithioesters **7** can be regarded as thiolation type reactions using elemental sulfur followed by alkylation. Activated methyl ketones such as acyl halides[17,18], diazomethyl ketones[19], β-ketosulfones[20] and N-(β-oxo-alkyl)-pyridinium iodides[21] are generally used as starting compounds. A few alternative methods can also be found[22,23]. Our new route to obtain the 2-oxo dithioesters **7** is the simple hydrolysis of the carbonyl analogous 2-iminium dithioester salts **6** accompanied by the energetically advantageous formation of an ammonium salt. One can start directly from the dithioacetates **1** without isolation of **6**. Alkylation of **1** in chloroform and subsequent hydrolysis was only an acceptable way for **7a** and **b**. However, using acetonitrile, also **7c–e** could also be obtained in very good yields (Scheme 3). The synthetic approach is clearly superior to the thiolation type reactions cited above. This is due to the fact that the 2-oxo dithioesters **7** are easily available in large



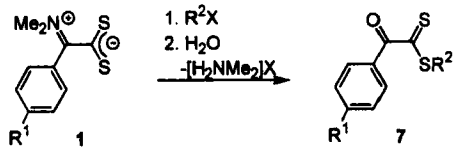
1 **6**

comp.	NR^2_2	R^1	comp.	NR^2_2	R^1	R^3	X	yield [%]
1a	NMe_2	H	**6a**	NMe_2	H	Me	I	95
1b	NMe_2	Me	**6b**	NMe_2	H	Et	I	88
1c	NMe_2	tBu	**6c**	NMe_2	Me	Me	I	95
1d	NMe_2	Ph	**6d**	NMe_2	tBu	Me	I	94
1e	pyrrolidino	H	**6e**	NMe_2	Ph	Me	I	96
1f	piperidino	H	**6f**	pyrrolidino	H	Me	I	94
			6g	piperidino	H	Me	I	93
			6h	NMe_2	H	Me	BF_4	62
			6i	NMe_2	H	Me	OSO_3Me	not isolated
			6k	NMe_2	H	Bn	Br	not isolated

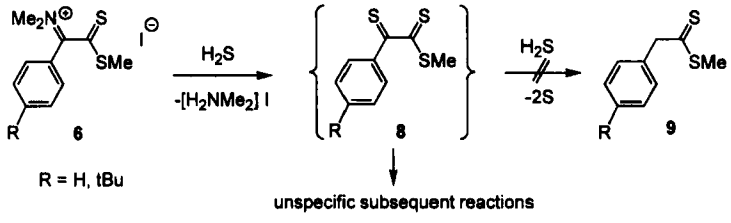
SCHEME 2

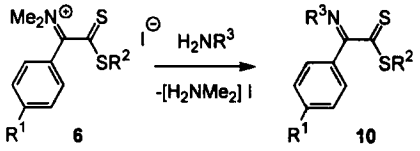
scale and higher yields without expensive purification, whereas in almost all precedent literature methods the isolation of the 2-oxo dithioesters requires column or thick layer chromatography or Kugelrohr distillation.

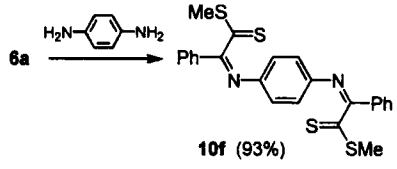
To the best of our knowledge, all attempts to yield the yet unknown 2-thioxo dithioesters by sulfurization (thionation) with phosphorus pentasulfide, Lawesson's or Davy's reagent[24] from the 2-oxo dithioesters **7** were without success[18,23,25]. In contrast to this, the reaction of the 2-iminium dithioester iodides **6** with hydrogen sulfide should offer a suitable route for the first synthesis of



comp.	R^1	R^2	R^2X	yield [%] $CHCl_3$	yield [%] MeCN
7a	H	Me	MeI / Me_2SO_4	86 / 86	-
7b	H	Et	EtI	80	-
7c	H	Bn	BnBr	29	90
7d	tBu	Me	MeI	51	95
7e	Ph	Me	MeI	37	97







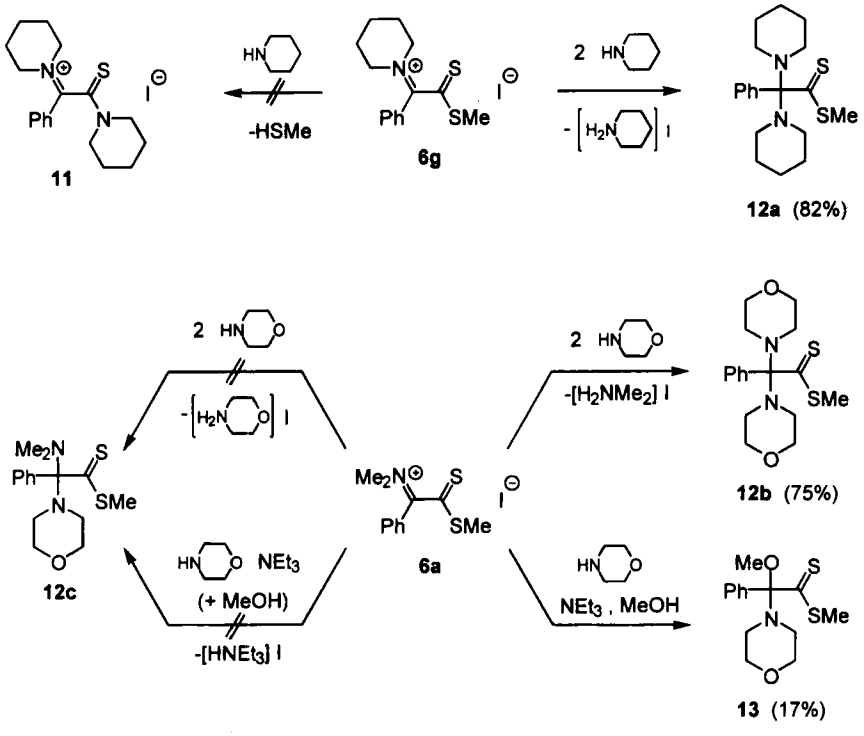
comp.	R^1	R^2	R^3	yield [%]
10a	H	Me	Ph	71
10b	H	Et	Ph	86
10c	tBu	Me	Ph	94
10d	tBu	Me	CN	79
10e	H	Me	NHPh	92

SCHEME 3

2-thioxo dithioesters **8**. The initial formation of the 2-thioxo dithioesters **8** is indicated by the formation of dimethylammonium iodide in consistently greater than 90% yield under all investigated reaction conditions. However, no 2-thioxo dithioester could be isolated as even at −78°C decomposition occurred. Unfortunately neither could any pure decomposition product be isolated and characterised. The formation of 2-aryl dithioacetic acid methyl esters **9** was not observed even if an excess of hydrogen sulfide was used (Scheme 3).

Having studied the reactivity of 2-iminium dithioester salts **6** with water and hydrogen sulfide, the analogous reaction with N-nucleophiles of the general type H_2NR was of interest. Using one equivalent of primary aromatic amines, cyanamide or phenyl hydrazine the reaction occured selectively at the iminium function of **6**. By this method the first synthesis of 2-imino-, 2-cyanimino- and 2-phenylhydrazono dithioesters **10** was achieved (Scheme 3). No thioamide was observed.

The reaction between **6g** and two equivalents of piperidine gives the 2,2-diamino dithioester **12a**, a novel type of aminals (Scheme 4). The unsymmetri-

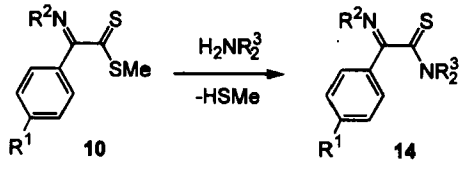


SCHEME 4

cally substituted dithioester **12c** should be obtained by reaction of **6a** with two equivalents of morpholine, but the only product isolated was the 2,2-dimorpholino dithioester **12b** resulting from the exchange of the amine substituents. The amine of higher basicity formed the ammonium salt in this case. An attempt was made to obtain **12c** using only one equivalent of morpholine and one equivalent of triethylamine to form the ammonium salt. In contrast to **12a** and **b** under the same conditions no precipitate was observed until the addition of methanol whereupon the unexpected 2-methoxy-2-morpholino dithioester **13** was obtained. Under these conditions (i.e. presence of amines) methanol is involved in the reaction, but compounds **6** are stable against pure methanol. **13** is a moisture sensitive hemi-aminal that decomposes to the related 2-oxo thiomorpholide, whereas **12a** and **b** are more stable.

In general, dithioesters react very rapidly with amines[26] in comparison with thiolo esters, thiono esters and normal esters [C(S)SR ≫ C(O)SR ~ C(S)OR ≫ C(O)OR]. The considerable steric hindrance of the dithioester group of **12** is illustrated by the fact that **12a** does not react with an excess of piperidine or ammonia. As expected, however, the 2-imino dithioesters **10** could be converted to the corresponding thioamides **14** (Scheme 5). For the synthesis of **14b** the dimethylamine was used as a complex with carbon dioxide (dimethylammonium dimethylcarbamate). This is a preferable method for the convenient stoichiometric use of dry and pure dimethylamine[27].

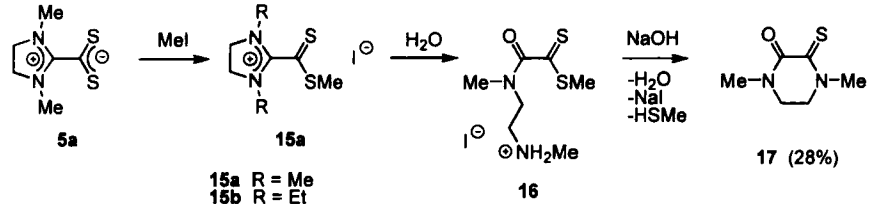
The synthesis of 1,4-dimethyl-3-thioxo piperazin-2-one **17**[28], a cyclic monothiooxamide confirmed the general validity of the new synthetic approach (Scheme 6). The first step being the transformation of the dithiocarboxylate **5a** to the dithioester **15a**. Reaction of **15a** with water gave the 1,1-dithiooxalic acid ester amide **16**, the amino group of which here forms the ammonium iodide. **16** was converted without isolation to the free amine, by an equimolar amount of sodium hydroxide, that immediately underwent intramolecular ring closure to



comp.	R^1	R^2	NR^3_2	yield [%]
14a	H	Ph	morpholino	74
14b	tBu	CN	NMe_2	44

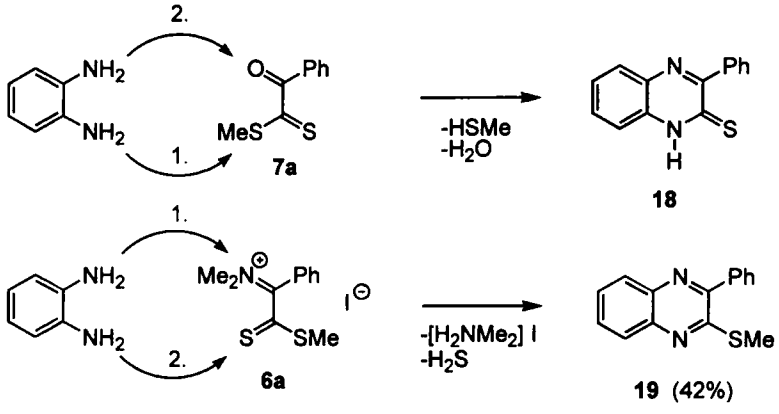
SCHEME 5

give **17** accompanied by elimination of methylthiol. Winberg and Coffman reported on the "*solubility in water*" of the 1,3-diethyl substituted compound **15b**[7]. This fact was obviously not recognized as a reaction to yield a 1,1-dithiooxalic acid ester amide (by analogy to **16**).



SCHEME 6

2-Oxo carboxylic acid derivatives are potential starting compounds for the synthesis of heterocycles. The reaction of the 2-oxo dithioester **7a** with *o*-phenylenediamine proceeds initially via formation of a thioamide, followed by ring closure to give 1,2-dihydroquinoxalin-2-thione **18**[29]. In the absence of bases the 2-methylthioquinoxaline **19** is only a byproduct. The change in the structure from **7a** to the iminium salt **6a** results in a change of reactivity of the carbon atoms C1 and C2. Consequently, after initial formation of the imine (2-imino dithioester), cyclization in this case can proceed with formation of an aromatic system by elimination of hydrogen sulfide and maintenance of the methylthio group to give **19** (Scheme 7). Because of the unspecific side reaction of hydro-



SCHEME 7

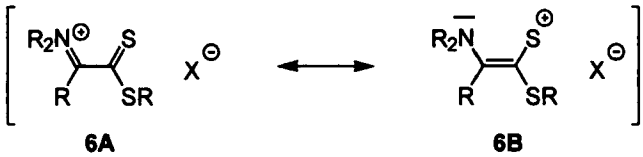
gen sulfide with **6a**, which has been already discussed, the yield is only moderate. This example is a good illustration of the reactivity of 2-iminio dithioester salts **6** which have been used as key compounds.

NMR-Studies and X-Ray Crystal Structure Analyses

In contrast to the 2-iminio dithioacetates **1** the routine n.m.r. spectra of numerous compounds **6** show a dynamic behavior, which is due to the rotation of the iminium function. The energy barrier for **6a** was estimated to be 63.9 ± 0.5 $kJ \cdot mol^{-1}$ by use of temperature dependent n.m.r. measurements and the Eyring equation: $\Delta G^{\neq} = RT_c[22.96 + \ln(T_c/\delta\upsilon)]$ $[J \cdot mol^{-1}]$.

An X-ray crystal structure determination of compound **6a** has been performed in order to elucidate, whether a strong polarization of the C=N double bond in **6A** and/or a significant contribution of the structure **6B** (in conjunction with a reduced bond order) is responsible for the observed low rotational barrier (Scheme 8).

The C2-N1 distance [1.290(7) Å] agrees exactly with the standard value of 1.29 Å for a $C(sp^2)$-$N(sp^2)$ double bond (see ref. 30), while the C1–S2 distance of 1.589(6) Å is even shorter than the corresponding standard value of 1.63 Å given in ref. 30 for a C-S double bond. The bond length C1–C2 [1.506(7) Å] approaches the standard value for a $C(sp^2)$-$C(sp^2)$ single bond [1.466 Å, ref. 30]. The distance between the iodide anion and the two atoms S2 and N1 is comparable and amounts to 3.857(2) and 3.766(5) Å, respectively. The dithiocarboxylate moiety is planar; the maximum deviation of an atom from a least-squares plane calculated including the four atoms C1, C2, S1, S2 amounts to 0.019(5) Å for C1. This group and the exactly planar dimethyliminium group $C[N(CH_3)_2)]$ make an interplanar angle of 79.2°. The dihedral angle between the plane of the phenyl ring and the approximately planar fragment formed by the atoms C1, C2, C3, C4, C5, N1 (maximum deviation from the l.s. plane of 0.120(7) Å observed for C4) amounts to 52.1°. According to the results of the X-ray structure analysis the bonding situation of **6a** is well described by the structure **6A** (Figure 1). The



6A **6B**

SCHEME 8

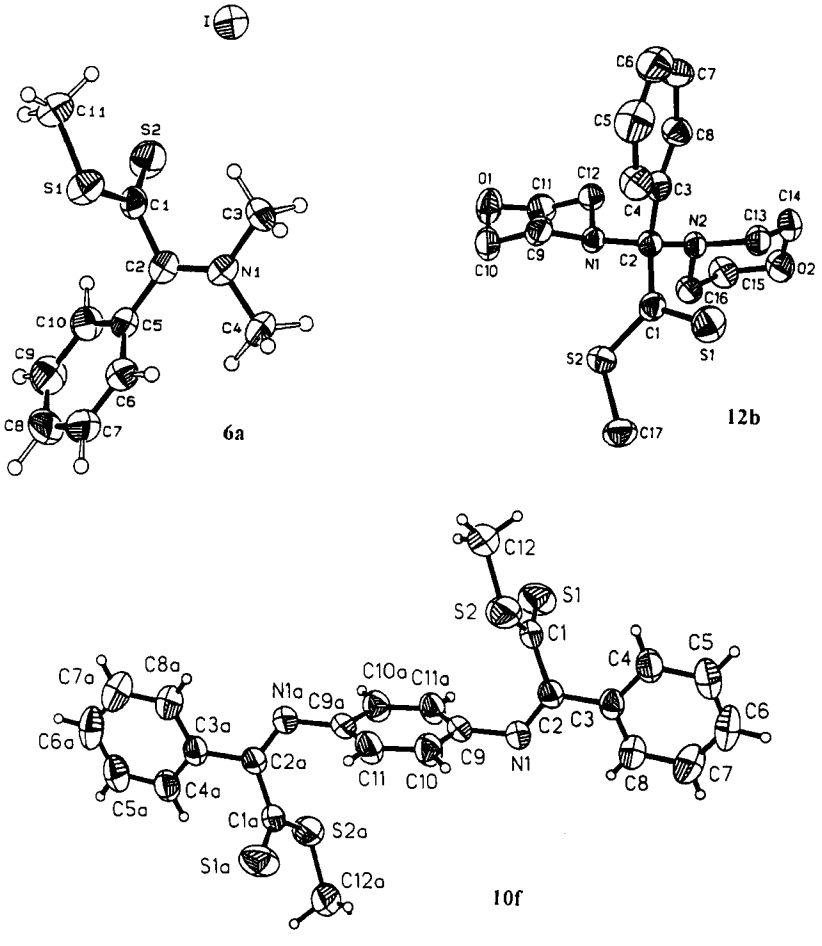


FIGURE 1 ORTEPII-Drawings of **6a**, **10f** and **12b** (Thermal Ellipsoids are Drawn at the 50% Level).

discussed geometrical and stereochemical parameters of **6a** are in good agreement with those observed for the closely related compound 2-dimethyliminio-2-phenyl dithioacetate **1a**[31].

The ^{1}H NMR spectra of the 2-phenylimino dithioesters **10a–c** show both Z- and E-isomers in the ratio of 6:1 (**10a, b**) and 10:1 (**10c**), respectively. In case of the bis(imino dithioester) **10f** the ratio of the symmetrical Z/Z-isomer to the Z/E-isomer is 2:1, whereas the E/E-isomer is not populated in an observable amount. If possible the signals of the less populated isomers are also given in the experimental part[32]. In contrast to this only one signal for the SMe-group was observed even down to −78°C for the 2-cyanimino dithioester **10d** and the 2-phenylhydrazono dithioester **10e**.

The crystal structure of **10f** is formed by centrosymmetrical molecules that are situated on the inversion center of the space group $P2_1/n$. Within the crystal the molecules are in the Z/Z configuration as is indicated by the relevant torsion angles (C9-N1-C2-C1 −0.7(5)° and C9-N1-C2-C3 177.2(3)°, respectively). The atoms C1, C2, C3, N1, C9 form a well approximated plane (largest deviation from a least-squares plane calculated including the five atoms amounts to 0.017(3) Å for C9). Both phenyl rings (C3-C8 and C9-C11A) and the dithioester group are exactly planar. The dihedral angles made-up between these planes and the above-mentioned one are 27.8°, 114.1° and 106.8°, respectively. The orientation of the two phenyl rings with respect to each other is approximately perpendicular. The corresponding interplanar angle amounts to 87.8°. Both atoms C1 and C2 are sp^2-hybridized having bond angle sums of 360.0° and 359.9°, respectively. The C2-N1 distance of 1.277(4) Å indicates clearly a double bond while the C1-C2, C2-C3 and C9-N1 distances of 1.501(4), 1.485(4) and 1.423(4) Å, respectively, correspond to single bonds. Within the crystal the molecules are held together by a very weak intermolecular hydrogen bond type interaction characterized by the following parameters: C12-H122 1.00(5), C12...N1 3.370(6), H122...N1 2.52(5) Å, C12-H122...N1 142(4)° (symmetry: 0.5-x, 0.5-y, 0.5-z). Furthermore, there is one short intermolecular S...S interaction observed (3.458(2) Å, symmetry: 1-x, -y, -z) that is shorter than the sum of the corresponding van der Waals-radii of 3.60 Å[33].

In the high resolution ^{13}C NMR spectra (125 MHz) of the 2,2-diamino dithioesters **12a** and **b** each carbon atom can be observed as a separate signal owing to the hindered rotation of the substituents at carbon C2. The substitution of only one morpholino group of **12b** by the smaller methoxy substituent (**13**) results in a decrease of the rotational barrier. This is expressed by the observation of four signals for the phenyl ring and two signals for the morpholino group at room temperature for the 2-methoxy-2-morpholino dithioester **13**.

Due to the four bulky substituents at the sp^3-hybridized atom C2 of **12b** a distorted tetrahedral arrangement around this atom is observed in the molecular structure. However, the mean value of the corresponding bond angles around C2 amounts to 109.4°. The distances of the C-N bonds of 1.486(4) for C2-N1 and 1.473(4) Å for C2-N2 are only little longer than the corresponding standard value of 1.47 Å for a $C(sp^3)$-$N(sp^3)$ bond[30]. Similarly, a lengthening of the corresponding C-C distances (C1-C2 1.556(4) Å, C2-C3 1.526(4) Å), compared to the standard value of 1.51 Å for a $C(sp^3)$-$C(sp^2)$ bond[30], is observed and especially pronounced in the case of the C1-C2 bond. The dithioester group is largely planar, the relevant S1-C1-S2-C17 torsion angle amounts to 2.5(3)°. Both morpholine rings exhibit a slightly distorted chair conformation. This is shown by the results of a ring puckering analysis[34]. The puckering parameters of

the first ring (N1 to C12) are q2 = 0.080(3), q3 = −0.589(3), Φ2 = −170(3)°, Q = 0.595(3) and θ = 172.3(3)°, while those for the second one (N2 to C16) are q2 = 0.048(3), q3 = −0.590(3), Φ2 = −178(4)°, Q = 0.592(3) and θ = 175.4(3)°, respectively. For an ideal cyclohexane chair conformation the Q value would be 0.63 Å (for R_{C-C} = 1.54 Å). The magnitude of the distortion is described by θ which is 7.7° for the first ring and 4.6° for the second one (or better by tanθ which is very small)[34]. The direction of the distortion, given by the Φ value (close to 180° in both cases) corresponds to a distortion of both the morpholine chairs towards a boat conformation.

Summary

Starting from the title compounds **1** the reactive 2-iminium-dithioester salts **6** are available by simple alkylation. These new iminium salts served as key components in further syntheses of several sulfur and nitrogen analogues of 2-oxo carboxylic acids. The high reactivity of the iminium function of **6** allows selective reactions with primary and secondary amines in presence of a dithioester group, forming 2-imino and 2,2-diamino dithioesters **10** and **12**, respectively. X-ray structure determinations of these new classes of dithioesters are included. The higher reactivity of the iminium function in **6a** versus the carbonyl group of the related 2-oxo-dithioester **7a** is also expressed by the model reactions with the 1,4-dinucleophilic *o*-phenylene diamine, which result in different products, 1,2-dihydro quinoxalin-2-thione **18** and 2-methylthio quinoxaline **19**. A synthesis of the cyclic monothiooxamide **17** is presented to emphasize that the synthetic strategy is generally applicable to compounds of the diaminocarbenium dithiocarboxylate type **4** and **5**.

EXPERIMENTAL

General Remarks

Melting points were determined with a Boetius hot plate microscope and are uncorrected. IR spectra were run on Bruker IFS 25 and Carl Zeiss Jena M 80, Specord 71 IR spectrophotometers. NMR spectra were recorded on Bruker AC 80, WP 200 and Varian 500 instruments, the deuterated solvents were dried with molecular sieve A4. Mass spectra were taken on an Intectra AMD 402 instrument. Elemental analyses were obtained on Carlo Erba Analysator 1102 and

Leco CHNS-932 instruments. X-ray measurements were performed on a Stoe STADI4 diffractometer. Column chromatography was performed on Merck silica gel 60 (70–200 mesh ASTM). With the exception of the syntheses of **7**, **14** and **17** all reactions were performed under an inert atmosphere of dry argon. All solvents were dried by standard methods, the quality referring to water traces was checked by Karl-Fischer-Titration. The Karl-Fischer-Titrations were run on a Mitsubishi moisturemeter Model CA-02 using the reagent Hydranal-Coulomat AD (Riedel-de Haën).

Syntheses

We recently reported[1] the synthesis of the starting compounds **1**. The *4,5-Dihydro-1,3-dimethyl-1H-imidazolium dithiocarboxylate* **5a** was synthesized as described in ref. 9.

2-Iminium Dithioester Iodide 6—General Procedure

To a stirred suspension of the pulverized 2-iminio-dithioacetates **1** (10 mmol) in 10 ml of acetonitrile the corresponding alkyl iodide (11 mmol) was added. The stirring was stopped when the crystallization of product started after 10–30 min. After 2 h (**6b**: 24 h) the reaction mixture was cooled for 1 h to −20°C and was filtered off under argon atmosphere. The filtrate was worked-up once to increase the yield. The products were stored under argon at 4°C. **6b**, **d**, **e** were recrystallized from acetonitrile in the range of 40°C to −20°C.

Dimethyl-[(Methylthio-Thiocarbonyl)-Phenyl-Methylene]-Ammonium Iodide (**6a**)

yield: 3.34 g (95%) red-violet crystals, m. p. 120°C (decomp.).–IR ($CHCl_3$): ν = 2945 cm^{-1}, 2760, 1650, 1235 (C═S), 1120, 1050, 1025, 690, 660.–^1H NMR ($CDCl_3$, 80 MHz): δ = 2.83 (s, 3H, SCH_3), 3.93 [s, 6H, $N(CH_3)_2$], 7.46–7.67 (m, 3H, ArH), 8.01–8.14 (m, 2H, ArH).–^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 19.2 (SCH_3), 47.9, 48.1 (NCH_3, broad), 128.1, 129.2 (aromat. C-2, C-6 and C-3, C-5), 128.4 (aromat. C_{quart}), 133.3 (aromat. C-4), 179.5 (C═N), 216.9 (C═S).–$C_{11}H_{14}INS_2$ (351.3): calcd. C 37.61, H 4.02, N 3.99, S 18.26; found C 37.79, H 3.90, N 4.00, S 18.29.

***[(Ethylthio-Thiocarbonyl)-Phenyl-Methylene]-Dimethyl-Ammonium Iodide* (6b)**

yield: 3.20 g (88%) red-brown crystals, m. p. 132–134°C (decomp.).–IR ($CHCl_3$): ν = 2945 cm^{-1}, 2750, 1650, 1450, 1230 (C═S), 1120, 1050, 1025, 700, 665.–^1H NMR ($CDCl_3$, 200 MHz): δ = 1.37 (t, J = 7.5 Hz, 3H, CH_2CH_3), 3.65 (q, J = 7.5 Hz, 2H, SCH_2), 3.89 [s, 6H, $N(CH_3)_2$], 7.54–7.58 (m, 3H, ArH), 8.07 (d, J = 8.3 Hz, 2H, ArH).–^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 11.9 (CH_2CH_3) 30.9 (SCH_2), 47.9, 48.6 (broad, NCH_3), 128.4, 129.6 (aromat. C-2, C-6 and C-3, C-5), 128.6 (aromat. C_{quart}), 133.7 (aromat. C-4), 179.1 (C═N), 216.4 (C═S).–$C_{12}H_{16}INS_2$ (365.3): calcd. C 39.46, H 4.41, N 3.83, S 17.56; found C 39.23, H 4.68, N 3.83, S 17.58.

***Dimethyl-[(4-Methyl-Phenyl)-(Methylthio-Thiocarbonyl)-Methylene]-Ammonium Iodide* (6c)**

yield: 3.47 g (95%) red crystals, m. p. 158–160°C (decomp.).–IR ($CHCl_3$): ν = 2955 cm^{-1}, 2755, 1650, 1610, 1235 (C═S), 1120, 1045, 1030.–^1H NMR ($CDCl_3$, 200 MHz): δ = 2.41 (s, 3H, $ArCH_3$), 2.80 (s, 3H, SCH_3), 3.90 [s, 6H, $N(CH_3)_2$], 7.34 (d, J = 8.2 Hz, 2H, ArH), 7.95 (d, J = 8.2 Hz, 2H, ArH).–^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 19.5 (SCH_3), 21.8 ($ArCH_3$), 47.9, 48.3 (NCH_3, broad), 125.8 (aromat. C-1), 129.0, 130.3 (aromat. C-2, C-6 and C-3, C-5), 145.5 (aromat. C-4), 180.4 (C═N), 218.6 (C═S).–$C_{12}H_{16}INS_2$ (365.3): calcd. C 39.46, H 4.41, N 3.83, S 17.56; found C 39.23, H 4.67, N 3.96, S 17.46.

***[(4-Tert.Butyl-phenyl)-(Methylthio-Thiocarbonyl)-Methylene]-Dimethyl-Ammonium Iodide* (6d)**

Yield: 3.84 g (94%) orange crystals, m. p. 156°C (decomp.).–IR ($CHCl_3$): ν = 2965 cm^{-1}, 2755, 1640, 1600, 1230 (C═S), 1125, 1110, 1050, 1030.–^1H NMR ($CDCl_3$, 200 MHz): δ = 1.31 (s, 9H, tBu), 2.81 (s, 3H, SCH_3), 3.89 [s, 6H, $N(CH_3)_2$], 7.55 (d, J = 8.7 Hz, 2H, ArH), 8.01 (d, J = 8.7 Hz, 2H, ArH).–^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 19.0 (SCH_3), 30.4 [$C(CH_3)_3$], 34.8 [$C(CH_3)_3$], 47.4, 48.2 (NCH_3), 125.1 (aromat. C_{quart}), 126.0, 128.4 (aromat. C-2, C-6 and C-3, C-5), 157.5 (aromat. C-4), 179.2 (C═N), 216.9 (C═S).–$C_{15}H_{22}INS_2$ (407.4): calcd. C 44.23, H 5.44, N 3.44, S 15.74; found C 44.26, H 5.29, N 3.60, S 15.66.

***Dimethyl-[(Methylthio-Thiocarbonyl)-(4-Phenyl-Phenyl)-Methylene]-Ammonium Iodide* (6e)**

yield: 4.11 g (96%) red crystals, m. p. 180–186°C (decomp.).–IR (KBr): ν = 2970 cm^{-1}, 1645, 1600, 1300, 1200, 1120, 1045, 1020, 770, 690.–^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.84 (s, 3H, SCH_3), 3.93 [s, 6H, $N(CH_3)_2$], 7.45–7.60 (m, 5H, C_6H_5), 7.78 (d, J = 8.5 Hz, 2H, ArH), 8.17 (d, J = 8.5 Hz, 2H, ArH).–$C_{17}H_{18}INS_2$ (427.4): calcd. C 47.78, H 4.25, N 3.28, S 15.01; found C 47.50, H 4.10, N 3.41, S 15.20.

***N-[(Methylthio-Thiocarbonyl)-Phenyl-Methylene]-Pyrrolidinium Iodide* (6f)**

yield: 3.56 g (94%) red crystals, m. p. 115–117°C (decomp.).–IR ($CHCl_3$): ν = 2940 cm^{-1}, 1635, 1450, 1230 (C═S), 1050, 695, 665.–^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.23 (quint, J = 6.7 Hz, 2H, NCH_2CH_2), 2.38 (quint, J = 5.2 Hz, 2H, NCH_2CH_2), 2.78 (s, 3H, SCH_3), 4.26–4.35 [m, 4H, $N(CH_2)_2$], 7.45–7.63 (m, 3H, ArH), 8.11 (d, J = 7.6 Hz, 2H, ArH).–^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 18.7 (SCH_3), 24.0, 24.4 (NCH_2CH_2), 56.3, 58.3 (NCH_2), 127.7, 128.9 (aromat. C-2, C-6 and C-3, C-5), 129.0 (aromat. C_{quart}) 133.2 (aromat. C-4), 175.3 (C═N), 217.0 (C═S).–$C_{13}H_{16}INS_2$ (377.3): calcd. C 41.38, H 4.27, N 3.71, S 17.00; found C 40.98, H 4.03, N 3.62, S 17.49.

***N-[(Methylthio-Thiocarbonyl)-Phenyl-Methylene]-Piperidinium Iodide* (6g)**

yield: 3.65 g (93%) red crystals, m. p. 142–144°C (decomp.).–IR ($CHCl_3$): ν = 2940 cm^{-1}, 2870, 1630, 1445, 1300, 1220 (C═S), 1040.–^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.80–2.12 [s, broad, 6H, $NCH_2(CH_2)_3$], 2.79 (s, 3H, SCH_3), 4.27–4.53 [d, broad, 4H, $N(CH_2)_2$], 7.48–7.60 (m, 3H, ArH), 8.01 (dd, J = 7.9 Hz, J = 1.4 Hz, 2H, ArH).–^{13}C NMR ($CDCl_3$, 20.1 MHz): δ = 19.8 (SCH_3), 22.0 [$N(CH_2)_2CH_2$], 27.1 (NCH_2CH_2), 57.2 (NCH_2), 128.2 (aromat. C_{quart}), 128.0, 129.7 (aromat. C-2, C-6 and C-3, C-5), 133.5 (aromat. C-4), 177.3 (C═N), 216.6 (C═S).–$C_{14}H_{18}INS_2$ (391.3): calcd. C 42.97, H 4.64, N 3.58, S 16.39; found C 42.81, H 4.80, N 3.56, S 16.22.

***Dimethyl-[(Methylthio-Thiocarbonyl)-Methylidene]-Ammonium Tetrafluoroborate* (6h)**

To a stirred suspension of 1.05 g (5 mmol) of pulverized **1a** in 5 ml of acetonitrile was added successively 0.74 g (5 mmol) of trimethyloxonium tetrafluoroborate at −20°C. The reaction mixture was warmed to room temperature and

the solvent was evaporated *in vacuo*. The residue was recrystallized twice from dry diethyl ether/acetonitrile under argon; yield: 0.965 g (62%) light-red crystals, m. p. 95–105°C.–IR (KBr): ν = 1640 cm^{-1}, 1445, 1400, 1040 (broad), 765, 695.–^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.81 (s, 3H, SCH_3), 3.76 (s, 3H, NCH_3), 3.81 (s, 3H, NCH_3), 7.50–7.67 (m, 3H, ArH), 7.75–7.80 (m, 2H, ArH).–$C_{11}H_{14}NS_2BF_4$ (311.2): calcd. C 42.46, H 4.53, N 4.50, S 20.61; found C 41.08, H 4.78, N 4.75, S 19.79[35].

2-Oxo-2-Phenyl-Dithioacetic Acid Methyl Ester (7a)

Method 1: To a stirred suspension of 5.23 g (25 mmol) of pulverized **1a** in 50 ml of $CHCl_3$ 3.83 g (27 mmol) of methyl iodide was added. After stirring for 1.5 h 100 ml of water was added and the reaction mixture was stirred vigorously for further 3 h. The aqueous layer was extracted with 50 ml of $CHCl_3$, the combined organic layers were washed twice with 50 ml of water and dried over Na_2SO_4. The solvent was evaporated *in vacuo*. The residue was purified by recrystallization from methanol or distillation *in vacuo* (b. p. 110°C/0.15 Torr). Method 2: To a stirred suspension of 5.23 g (25 mmol) of pulverized **1a** in 50 ml of $CHCl_3$ 3.15 g (25 mmol) of dimethyl sulfate was added. The reaction mixture was refluxed for 3 h, whereafter the procedure is analogous to method 1; yield in each case (method 1 and 2): 4.22 g (86%) red crystals, m. p. 32–33°C. The m. p. and the spectrometric data correspond to those of ref. 17–19.

2-Oxo-2-Phenyl-Dithioacetic Acid Ethyl Ester (7b)

To a stirred suspension of 5.23 g (25 mmol) of pulverized **1a** in 50 ml of $CHCl_3$ 4.21 g (27 mmol) of ethyl iodide was added. The reaction mixture was refluxed for 1.5 h. 100 ml of water was added and the reaction mixture was stirred vigorously for 3 h. The aqueous layer was extracted with 50 ml of $CHCl_3$, the combined organic layers were washed twice with 50 ml of water and dried over Na_2SO_4. The solvent was evaporated *in vacuo*. The residue was purified by column chromatography with $CHCl_3$; yield: 4.20 g (80 %) red oil. The spectrometric data correspond to those of ref. 18.

2-Oxo-2-Phenyl-Dithioacetic Acid Benzyl Ester (7c) *and* *2-Oxo-2-(4-Phenyl-Phenyl)-Dithioacetic Acid Methyl Ester* (7e)

To a stirred suspension of 10 mmol of the corresponding pulverized 2-iminio dithioester **1** in 10 ml of acetonitrile 1.71 g (10 mmol) of benzyl bromide or 1.56

g (11 mmol) of methyl iodide was added. After stirring for 1.5 h, 5 ml of water was added and the reaction mixture was stirred for further 3 h to precipitate the product. After addition of 30 ml of water the solid was filtered off, washed three times with 20 ml of water and dried. The crude product was recrystallized from methanol. **7c**: yield: 2.45 g (90 %) orange crystals, m. p. 33°C. The spectrometric data correspond to those of ref. 18 (m. p. 34°C). **7e**: yield: 2.65 g (97 %) orange crystals, m. p. 87–88°C (analogous to ref. 17).

2-(4-Tert. Butyl-Phenyl)-2-Oxo-Dithioacetic Acid Methyl Ester (7d)

To a stirred suspension of 2.65 g (10 mmol) of pulverized **1c** in 10 ml of acetonitrile 1.56 g (11 mmol) of methyl iodide was added. After stirring for 24 h, 5 ml of water was added and the reaction mixture was stirred for further 3 h. The solvent was evaporated *in vacuo* and the residue was partitioned between 30 ml of $CHCl_3$ and 30 ml of water. The organic phase was washed twice with 30 ml of water, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was recrystallized from methanol; yield: 2.41 g (95%) red crystals, m. p. 32°C.–IR (KBr): ν = 1660 cm^{-1} (C═O), 1595, 1400, 1260 (C═S), 1120, 1040, 845, 685.–^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.32 (s, 9H, tBu), 2.81 (s, 3H, SCH_3), 7.46 (d, J = 8.6 Hz, 2H, ArH), 7.95 (d, J = 8.6 Hz, 2H, ArH).–MS (70 eV): *m/z* (%) = 252 (10) [M^+], 161 (100) [M^+-CSSMe], 146 (14) [M^+-CSSMe-Me].–$C_{13}H_{16}OS_2$ (252.4): calcd. C 61.86, H 6.39, S 25.41; found C 61.60, H 6.33, S 25.71.

2-Imino Dithioester 10a, c, f, *and 2-Cyanimino Dithioester* 10d*—General Procedure*

To a stirred suspension of 10 mmol of **6** in 5 ml of acetonitrile was added dropwise a solution of 0.93 g (10 mmol) aniline (**10a**, **c**), 0.42 g (10 mmol) cyanamide (**10d**) or 0.54 g (5 mmol) *p*-phenylene diamine (**10f**) in 10 ml of acetonitrile. The reaction mixture was stirred for 1 h to precipitate the product. After cooling to −78°C for 1 h the solid was filtered off, washed three times with 20 ml of water and dried. The crude product was recrystallized from methanol/acetone. The mother liquor was worked-up once.

2-Phenyl-2-Phenylimino-Dithioacetic Acid Methyl Ester (10a)

yield: 1.93 g (71%) orange crystals, m. p. 62–63°C.–IR (KBr): ν = 1600 cm^{-1}, 1580, 1565, 1260, 1185, 1105, 1020, 1005, 745, 680.–^{1}H NMR ($CDCl_3$,

200 MHz): Z-isomer: δ = 2.59 (s, 3H, SCH_3), 6.88 (dd, J = 8.3 Hz, J = 1.2 Hz, 2H, N-ArH), 7.00 (tt, J = 7.4 Hz, J = 1.3 Hz, 1H, N-ArH), 7.23 (t, J = 7.7 Hz, 2H, N-ArH), 7.41–7.46 (m, 3H, ArH), 7.94 (dd, J = 7.9 Hz, J = 1.8 Hz, 2H, ArH), E-isomer: δ = 2.71 (s, SCH_3).–MS (70 eV): *m/z* (%) = 271 (2) [M^+], 180 (100) [M^+-CSSMe].–$C_{15}H_{13}NS_2$ (271.4): calcd. C 66.38, H 4.83, N 5.16, S 23.63; found C 65.39, H 4.82, N 5.22, S 23.91.

2-(4-Tert.Butyl-Phenyl)-2-Phenylimino-Dithioacetic Acid Methyl Ester (10c)

yield: 3.09 g (94%) orange crystals, m. p. 103–105°C.–IR (KBr): ν = 2930 cm^{-1}, 1585, 1575, 1185, 1120, 995, 850, 760, 685, 660.–^{1}H NMR ($CDCl_3$, 200 MHz): Z-isomer: δ = 1.33 (s, 9H, tBu), 2.57 (s, 3H, SCH_3), 6.87 (dd, J = 8.3 Hz, J = 1.1 Hz, 2H, N-ArH), 6.99 (t, J = 8 Hz, 1H, N-ArH), 7.22 (t, J = 7.7 Hz, 2H, N-ArH), 7.44 (dt, J = 8.6 Hz, J = 2.1 Hz, 2H, ArH), 7.87 (dt, J = 8.5 Hz, J = 2.1 Hz, 2H, ArH), E-isomer: δ = 1.24 (s, tBu), 2.71 (s, SCH_3).–^{13}C NMR ($CDCl_3$, 50.3 MHz): Z-isomer: δ = 18.8 (SCH_3), 31.1 [$C(CH_3)_3$], 34.9 [$C(CH_3)_3$], 119.8 (aromat. CH, N-Ph), 123.5 (aromat. C-4, N-Ph), 125.3 (aromat. CH), 128.2 (aromat. CH, overlapped), 132.7 (aromat. C-1, Ph), 149.8 (aromat. C_{quart}, N-Ph), 154.9 (aromat. C-4, Ph), 166.7 (C═N), 228.4 (C═S).–MS (70 eV): *m/z* (%) = 327 (2) [M^+], 236 (100) [M^+-CSSMe], 221 (16) [M^+-CSSMe-Me].–$C_{19}H_{21}NS_2$ (327.5): calcd. C 69.68, H 6.46, N 4.28; found C 69.34, H 6.34, N 4.10.

2-(4-Tert.Butyl-Phenyl)-2-Cyanimino-Dithioacetic Acid Methyl Ester (10d)

yield: 2.19 g (79%) orange crystals, m. p. 125–126°C.–IR (KBr): ν = 2940 cm^{-1}, 2170 (CN), 1530, 1285, 1050, 840, 665.–^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.32 (s, 9H, tBu), 2.89 (s, 3H, SMe), 7.47 (d, J = 7.8 Hz, 2H, ArH), 7.89 (d, J = 8.6 Hz, 2H, ArH).–^{13}C NMR ($CDCl_3$, 20.1 MHz): δ = 19.0 (SCH_3), 30.9 [$C(CH_3)_3$], 35.5 [$C(CH_3)_3$], 113.1 (N-CN), 126.2, 130,4 (aromat. C-2, C-6 and C-3, C-5) 129.3 (aromat. C-1), 160.1 (aromat. C-4), 187.0 (C═N), 223.3 (C═S).–MS (70 eV): *m/z* (%) = 278 (8) [M^+ + 2], 276 (2) [M^+], 261 (6) [M^+-Me], 220 (100) [M^+-MeNHCN], 205 (27) [M^+-MeNHCN-Me], 185 (89) [M^+-CSSMe], 170 (32) [M^+-CSSMe-Me], 91 (42) [$CSSMe^+$].–$C_{14}H_{16}N_2S_2$ (276.4): calcd. C 60.83, H 5.83, N 10.13, S 23.20; found C 61.17, H 5.99, N 10.21, S 23.53.

N,N'-Bis[(Methylthio-Thiocarbonyl)-Phenyl-Methylen]-1,4-Phenylene Diamine (10f)

yield: 4.33 g (93 %) red crystals, m. p. 150–152°C.–IR (KBr): ν = 1590 cm^{-1}, 1540, 1190, 1110, 1030, 865, 685.–^{1}H NMR ($CDCl_3$, 500 MHz): Z/Z-isomer: δ = 2.63 (s, 6H, SCH_3), 6.83 (s, 4H, N-ArH), 7.44 (t, J = 7.5 Hz, 4H, ArH), 7.48–7.52 (m, 2H, ArH), 7.95 (d, J = 8.8 Hz, 4H, ArH), Z/E-isomer: δ = 2.58 (s, 3H, Z-SCH_3), 2.73, (s, 3H, E-SCH_3), 6.71 (d, J = 8.8 Hz, 2H, N-ArH), 6.75 (d, J = 8.6 Hz, 2H, N-ArH).–^{13}C NMR ($CDCl_3$, 125.7 MHz): Z/Z-isomer: δ = 18.9 (SCH_3), 120.0 (aromat. CH, NC_4H_4N), 128.4 (aromat. CH, Ph), 131.3 (aromat. C-4, Ph), 135.5 (aromat. C_{quart}, Ph), 150.0 (aromat. C_{quart}, NC_4H_4N), 167.2 (C═N), 228.8 (C═S), Z/E-isomer: δ = 18.8, 19.8 (SCH_3), 120.2, 121.7 (aromat. CH, NC_4H_4N), 135.1, 135.4 (aromat. C_{quart}, Ph), 144.6, 147.1 (aromat. C_{quart}, NC_4H_4N), 166.5 (C═N) 167.2 (C═N, overlapped by Z/Z-isomer), 228.2, 229.1 (C═S).–MS (70 eV): *m/z* (%) = 464 (11) [M^+], 373 (100) [M^+-CSSMe], 327 (14) [M^+-CSSMe-CH_2S], 224 (20) [M^+-N═C(Ph)CSSMe-CH_2S], 223 (18) [M^+-N═C(Ph)CSSMe-SMe], 179 (28) [M^+-N═(Ph)CSSMe-CSSMe], 141 [M-2CSSMe^{++}].–$C_{24}H_{20}N_2S_4$ (464.7): calcd. C 62.03, H 4.34, N 6.03, S 27.60; found C 62.20, H 4.35, N 6.08, S 27.72.

2-Phenyl-2-Phenylimino-Dithioacetic Acid Ethyl Ester (10b)

To a stirred suspension of 3.65 g (10 mmol) of **6b** in 5 ml of acetonitrile was added dropwise a solution of 0.93 g (10 mmol) aniline in 10 ml of acetonitrile. The reaction mixture was stirred for 1 h. The solvent was evaporated and the residue was partitioned between 30 ml of $CHCl_3$ and 30 ml of water. The organic phase was washed twice with 30 ml of water, dried over $CaCl_2$ and concentrated *in vacuo*. The residue was purified twice by column chromatography with toluene; yield: 2.45 g (86%) red-brown oil.–IR (CCl_4): ν = 3055 cm^{-1}, 2955, 2910, 1605, 1590, 1195, 1120, 1010, 845, 690.–^{1}H NMR ($CDCl_3$, 200 MHz): Z-isomer: δ = 1.11 (t, J = 7.4 Hz, 3H, CH_3), 3.20 (q, J = 7.4 Hz, 2H, CH_2), 6.90 (dd, J = 7.4 Hz, J = 1.2 Hz, 2H, N-ArH), 7.01 (tt, J = 7.4 Hz, J = 1.4 Hz, 1H, N-ArH), 7.23 (t, J = 7.6 Hz, 2H, N-ArH), 7.42–7.47 (m, 3H, ArH), 7.97 (dd, J = 7.9 Hz, J = 1.7 Hz, 2H, ArH), E-isomer: δ = 1.42 (t, J = 7.5 Hz, CH_3), 3.30 (q, J = 7.5 Hz, CH_2).–^{13}C NMR ($CDCl_3$, 20.1 MHz): δ = 12.1 (CH_3), 21.6 (CH_2), 120.1 (aromat. CH, N-Ph), 128.4 (aromat. CH), 123.8 (aromat. C-4, N-Ph), 128.6 (aromat. CH, overlapped), 131.5 (aromat. C-4, Ph), 135.7 (aromat. C_{quart}, Ph), 150.0 (aromat. C_{quart}, N-Ph), 166.9 (C═N), 227.7 (C═S).–MS (70 eV): *m/z* (%) = 285 (2) [M^+], 180 (100) [M^+-CSSEt].–

$C_{16}H_{15}NS_2$ (285.4): calcd. C 67.33, H 5.30, N 4.91, S 22.47; found C 67.25, H 5.42, N 4.77, S 22.51.

2-Phenyl-2-Phenylhydrazono-Dithioacetic Acid Methyl Ester (**10e**)

To a stirred suspension of 3.51 g (10 mmol) of **6a** in 5 ml of acetonitrile was added dropwise a solution of 1.08 g (10 mmol) phenyl hydrazine in 10 ml of acetonitrile. The reaction mixture was stirred for 1 h. The solvent was evaporated and the residue was partitioned between 30 ml of $CHCl_3$ and 30 ml of water. The organic phase was washed twice with 30 ml of water, dried over $CaCl_2$ and concentrated *in vacuo*. The residue was purified by column chromatography with toluene to give 2.80 g (98%) of a red oil, which crystallized. The product was recrystallized from methanol/acetone; yield: 2.64 g (92%) intensive red crystals, m. p. approx. 72–82°C[36].–IR (KBr): ν = 3215 cm^{-1} (NH), 1590, 1525, 1470, 1245, 1195, 1105, 1040, 745, 680.–^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.66 (s, 3H, SCH_3), 6.99 (t, J = 7 Hz, 1H, ArH), 7.17–7.58 (m, 9H, ArH), 7.80 (s, 1H, NH).–^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 18.5 (SCH_3), 114.4 (aromat. C-2, C-6, N-Ph), 122.7 (aromat. C-4, N-Ph), 129.32, 129.40, 129.45 (aromat. CH), 129.48 (aromat. C-4, Ph), 131.8 (aromat. C_{quart}, Ph), 142.5, 147.4 (aromat. C_{quart}, N-Ph and C=N), 221.7 (C=S).–MS (70 eV): *m/z* (%) = 286 (70) [M^+], 271 (100) [M^+-Me], 239 (29) [M^+-SMe], 195 (11) [M^+-CSSMe], 77 (89) [Ph^+].–$C_{15}H_{14}N_2S_2$ (286.4): calcd. C 62.90, H 4.93, N 9.78, S 22.39; found C 62.60, H 4.90, N 9.75, S 22.70.

2-Phenyl-2,2-Dipiperidino-Dithioacetic Acid Methyl Ester (**12a**)

To a stirred suspension of 3.91 g (10 mmol) of **6g** in 5 ml of acetonitrile was added dropwise 1.70 g (20 mmol) of piperidine. The reaction mixture was stirred with a strong magnetic stirrer or, if necessary, manually for 1h to precipitate the product. After cooling to −20°C the solid was filtered off, washed three times with 20 ml of water and dried. The product was recrystallized from acetone; yield: 2.86 g (82%) orange crystals, m. p. 125–127°C.–IR (KBr): ν = 2920 cm^{-1}, 2900, 2825, 2800, 1430, 1110, 1065, 1020, 1000, 985, 780, 700.–^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 1.02 (s, broad, 1H, CH-piperidino), 1.10–1.23 (m, 2H, CH-piperidino), 1.36–1.82 (m, 13H, CH-piperidino), 2.48 (d, broad, J = 11 Hz, 1H, CH-piperidino), 2.54 (s, 3H, SCH_3) 2.94 (d, broad, J = 10 Hz, 1H, CH-piperidino), 3.30 (s, broad, 2H, CH-piperidino), 7.18–7.24 (m, 2H, ArH), 7.26 (d, J = 7 Hz, 1H, ArH), 7.32 (t, J = 8 Hz, 1H, ArH), 7.52 (d, J = 8.0 Hz, 1H, ArH).–^{13}C NMR (CD_2Cl_2, 125.7 MHz): δ = 19.3 (SCH_3) 25.6, 25.8, 26.0,

26.7, 27.1, 27.6 [$NCH_2(CH_2)_3$], 47.69, 47.73, 50.3, 52.8 (NCH_2), 96.9 (NCN), 125.8, 126.5, 126.9, 127.6, 131.4 (aromat. CH), 134.6 (aromat. C_{quart}), 227.4 (C═S).–MS (70 eV): *m/z* (%) = 264 (5) [M^+-piperidino], 257 (100) [M^+-CSSMe].–$C_{19}H_{28}N_2S_2$ (348.6): calcd. C 65.47, H 8.10, N 8.04, S 18.40; found C 65.17, H 8.13, N 7.53, S 18.30.

2,2-Dimorpholino-2-Phenyl-Dithioacetic Acid Methyl Ester (12b)

To a stirred suspension of 3.51 g (10 mmol) of **6a** in 10 ml of acetonitrile was added dropwise 1.74 g (20 mmol) of morpholine. The reaction mixture was stirred for 10 min to precipitate the product. After cooling to −20°C for 1 h the solid was filtered off, washed three times with 20 ml of water and dried. The crude product was recrystallized from acetone; yield 2.64 g (75%) orange crystals, m. p. 157–160°C.–IR (KBr): ν = 2925 cm^{-1}, 2835, 2810, 1435, 1270, 1100, 1080, 995, 985, 865, 785, 710, 670, 555.–^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 1.52 (s, broad, 1H, NCH), 1.89 (s, broad, 2H, NCH), 2.15, (s, broad, 1H, NCH), 2.43 (s, broad, 1H, NCH), 2.58 (s, 3H, SCH_3), 2.84–2.91 (m, 1H, NCH), 3.12 (s, broad, 2H, NCH), 3.57–3.80 (m, 7H, OCH), 3.87 (s, broad, 1H, OCH), 7.23–7.30 (m, 3H, ArH), 7.37 (t, J = 7.2 Hz, 1H, ArH), 7.51 (d, J = 8.0 Hz, 1H, ArH).–^{13}C NMR (CD_2Cl_2, 125.7 MHz): δ = 19.2 (SCH_3), 47.0, 47.3, 48.8, 51.3 (NCH_2), 66.2, 67.2, 67.4, 67.8 (OCH_2), 95.0 (NCN), 126.1, 126.6, 127.2, 127.3, 131.2 (aromat. CH), 132.5 (aromat. C_{quart}), 225.8 (C═S).–MS (70 eV): *m/z* (%) = 266 (9) [M^+-morpholino], 261 (100) [M^+-CSSMe].–$C_{17}H_{24}N_2O_2S_2$ (352.5): calcd. C 57.92, H 6.86, N 7.94, S 18.19; found C 58.06, H 7.00, N 7.80, S 18.44.

2-Methoxy-2-Morpholino-2-Phenyl-Dithioacetic Acid Methyl Ester (13)

To a stirred suspension of 3.51 g (10 mmol) of **6a** in 5 ml of acetonitrile was added dropwise a solution of 0.87 g (10 mmol) of morpholine and 1.01 g (10 mmol) of triethyl amine in 15 ml of acetonitrile. The reaction mixture was stirred for 1 h. The solvent was evaporated and 10 ml of methanol was added. After storage at −20°C for 1 d, the solid was filtered off under argon. The product was recrystallized successively from dry methanol twice and hexane; yield: 0.515 g (17%) orange crystals, m. p. 125–128°C.–IR (KBr): ν = 2975 cm^{-1}, 2940, 2850, 1445, 1265, 1110, 1070, 990, 810, 760, 700.–^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.55 (s, 3H, SCH_3), 2.56–2.66 (m, 2H, NCH_2), 2.74–2.84 (m, 2H, NCH_2), 3.17 (s, 3H, OCH_3), 3.75–3.82 (m, 4H, OCH_2), 7.27–7.32 (m, 3H, ArH), 7.48–7.52 (m, 2H, ArH).–^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 19.5 (SCH_3), 48.0 (NCH_2), 51.6 (OCH_3), 67.6 (OCH_2), 102.8 (OCN), 127.4,

129.3 (aromat. C-2, C-6 and C-3, C-5), 128.3 (aromat. C-4), 137.3 (aromat. C_{quart}), 233.0 (C=S). MS (70 eV): *m/z* (%) = 206 (100) [M^+-CSSMe– $C_{14}H_{19}NO_2S_2$ (297.4) calcd. C 56.53, H 6.44, N 4.71, S 21.56; found C 56.26, H 6.39, N 4.81, S 21.68.

2-Phenyl-2-Phenylimino-Thioacetic Acid Morpholide (14a)

To a stirred suspension of 2.71 g (10 mmol) of **10a** in 10 ml of acetonitrile 0.87 g (10 mmol) of morpholine was added. After stirring for 1 h the solvent was evaporated. The residue was recrystallized from methanol; yield 2.29 g (74%) yellow crystals, m. p. 146–148°C.–IR (KBr): ν = 2930 cm^{-1}, 2840, 1595, 1575, 1480, 1415, 1260, 1230, 1095, 1015, 935, 750, 685.–^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.95–3.08 (m, 1H, morpholino), 3.35–3.50 (m, 4H, morpholino), 3.67–3.77 (m, 1H, morpholino), 4.00–4.22 (m, 2H, morpholino), 7.06–7.18 (m, 3H, N-ArH), 7.32 (t, J = 7.7 Hz, 2H, N-ArH), 7.43–7.51 (m, 3H, ArH), 7.96 (dd, J = 7.6 Hz, J = 2 Hz, 2H, ArH).–^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 46.7, 51.9 (NCH_2), 65.9, 66.0 (OCH_2), 120.3 (aromat. CH, N-Ph), 124.6 (aromat. C-4, N-Ph), 128.1, 128.5, 128.6 (aromat. CH), 131.3 (aromat. C-4, Ph), 135.4 (aromat. C_{quart}, Ph), 148.8 (aromat. C_{quart}, N-Ph), 161.6 (C=N), 193.0 (C=S).–MS (70 eV): *m/z* (%) = 310 (5) [M^+], 180 (100) [M^+–C(S)N(CH_2CH_2)$_2$O].– $C_{18}H_{18}N_2OS$ (310.4): calcd. C 69.65, H 5.84, N 9.02, S 10.33; found C 69.50, H 5.77, N 9.11, S 10.57.

2-(4-Tert.Butyl-Phenyl)-2-Cyanimino-Thioacetic Acid Dimethylamide (14b)

To a stirred suspension of 1.38 g (5 mmol) of **10d** in 5 ml of acetonitrile 0.347 g of distilled dimethyl ammonium dimethyl carbamate (containing 5 mmol of dimethyl amine: $HNMe_2$: CO_2 = 1.8:1) was added. After stirring for 1 h the solvent was evaporated *in vacuo*. The residue was recrystallized from methanol; yield: 599 mg (44%) yellow crystals, m. p. 181–183°C.–IR (KBr): ν = 2965 cm^{-1}, 2865, 2180 (CN), 1600, 1570, 1525, 1410, 1395, 1320, 1300, 1255, 1125, 1000, 845, 770, 520.–^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.32 (s, 9H, tBu), 3.22 (s, 3H, NCH_3), 3.58, (s, 3H, NCH_3), 7.47 (d, J = 6.8 Hz, 2H, ArH), 7.87 (d, J = 7.7 Hz, 2H, ArH).–^{13}C NMR ($CDCl_3$, 20.1 MHz): δ = 31.0 [C(CH_3)$_3$], 35.5 [C(CH_3)$_3$], 40.6, 42.4 (NCH_3), 113.7 (N-CN), 126.6, 130.0 (aromat. C-2, C-6 and C-3, C-5), 129.0 (aromat. C-1), 159.9 (aromat. C-4), 182.4 (C=N), 191.1 (C=S).–MS (70 eV): *m/z* (%) = 273 (49) [M^+], 258 [M^+-Me], 230 (70) [M^+-H_2C=NMe], 217 (77) [M^+-MeNHCN], 216 (74), 215 (62), 185 (11) [M^+-

$C(S)NMe_2]$, 88 (100) $[C(S)NMe_2^+]$.–$C_{15}H_{19}N_3S$ (273.4): calcd. C 65.90, H 7.00, N 15.37, S 11.73; found C 65.75, H 7.08, N 15.25, S 12.03.

4,5-Dihydro-1,3-Dimethyl-2-(Methylthio-Thiocarbonyl)-1H-Imidazolium Iodide (15)

To a stirred suspension of 1.74 g (10 mmol) of pulverized **5a** in 5 ml of THF 1.56 g (11 mmol) of methyl iodide was added. After stirring for 1 d the product was filtered off under argon. yield 3.15 g (99%) red crystals, m. p. 132–135°C (change of modification in the melting range 113–116°C).–IR (Nujol): ν = 1600 cm^{-1}, 1445, 1370, 1280, 1000.–^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.87 (s, 3H, SCH_3), 3.10 (s, 6H, NCH_3), 4.28 (s, broad, 4H, NCH_2).–^{13}C NMR ($CDCl_3$, 20.1 MHz): δ = 20.3 (SCH_3), 34.8 (NCH_3), 51.5 (NCH_2), 163.7 (NCN), 205.9 (C=S).–$C_7H_{13}IN_2S_2$ (316.2): calcd. C 26.59, H 4.14, N 8.86; found C 26.70, H 4.13, N 8.68.

1,4-Dimethyl-3-Thioxo-Piperazin-2-one (17)

To a stirred suspension of 871 mg (5 mmol) of pulverized **5a** in 5 ml of acetonitrile 780 mg (5.5 mmol) of methyl iodide was added. The mixture was stirred for 3 h meanwhile **15a·MeCN** crystallized. 2 ml of water was added and the solution was diluted with 25 ml of acetonitrile. To this orange colored solution 5 ml of a 1 M NaOH was added dropwise, whereby the color changed to yellow. The solvent was evaporated. The solid residue was stirred with 15 ml of $CHCl_3$ to give a suspension. After standing for 30 min the solid was filtered off and the filtrate was concentrated *in vacuo*. The residue was recrystallized from methanol; yield: 219 mg (28%) yellow crystals, m. p. 151–153°C.–IR (KBr): ν = 2950 cm^{-1}, 2900, 2860, 1655 (C=O), 1510, 1335, 1250, 1185, 1090, 985, 760, 575.–^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.07 [s, 3H, $C(O)NCH_3$], 3.49 [s, 3H, $C(S)NCH_3$], 3.53–3.59 [m, 2H, $C(O)NCH_2$], 3.67–3.74 [m, 2H, $C(S)NCH_2$].–MS (70eV): *m/z* (%) = 158 (100) $[M^+]$.–$C_6H_{10}N_2OS$ (158.2): calcd. C 45.55, H 6.37, N 17.71, S 20.27; found C 45.50, H 6.43, N 18.09, S 20.57.

2-Methylthio-3-Phenyl-Quinoxaline (19)

To a stirred suspension of 3.51 g (10 mmol) of **6a** in 10 ml of acetonitrile was added a solution of 1.08 g (10 mmol) of *o*-phenylene diamine in 5 ml of acetonitrile. The reaction mixture was stirred for 2 h to precipitate the product. The

solid was filtered off and recystallized twice from acetone; yield: 1.06 g (42%) colorless crystals, m.p. 135–136°C (ref. 37: 133–136°C).

X-Ray Crystal Structure Determination

Suitable single crystals of **6a** were obtained by slow recrystallization from dry methanol under argon atmosphere. Because of the moisture sensitivity of this compound the single crystal used for the diffractometer measurement was enclosed in a capillary. Single crystals of **10f** and **12b** were obtained by recrystallization from acetone and methanol, respectively. For the intensity measurement the crystals of these two compounds were glued on a glass fiber using apiezon

TABLE I Crystal data and details of the intensity measurement and structure refinement of **6a** **10f** and **12b**

Parameter	**6a**	**10f**	**12b**
Formula	$C_{11}H_{14}INS_2$	$C_{24}H_{20}N_2S_4$	$C_{17}H_{24}N_2O_2S_2$
Molecular weight [g·mol^{-1}]	351.27	464.68	352.51
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a[Å]	12.087(2)	10.708(2)	15.686(2)
b[Å]	10.219(1)	9.242(2)	12.427(2)
c[Å]	12.766(1)	12.424(2)	9.127(2)
β[°]	115.59(1)	108.65(3)	95.34(1)
V[Å^3]	1422.2	1165.0	1771.4
Z	4	2	4
F(000)	688	484	752
μ (MoK_α) [mm^{-1}]	2.48	0.42	0.31
D_x[g·cm^{-3}]	1.641	1.325	1.322
Crystal size [mm]	0.34·0.27·0.15	0.27·0.23·0.08	0.25·0.22·0.15
$2\theta_{max}$[°]	45	48	45
Reflections mesured	4599	4037	4905
unique	1817	1836	2313
observed	1582	1231	1584
with $I/\sigma(I)$	1.5	2.0	2.0
in the refinement	1582	1835[a,b]	2311[a,c]
Reflections/parameter	10.8	11.0	10.9
R	0.035	0.0436	0.0387
wR	0.022	0.1198	0.1021
S	4.57	1.049	1.083
Max. und min. residual electron density [e·Å^{-3}]	0.447 −0.412	0.25 −0.24	0.16 −0.20

[a]Refinement based on F^2 values using the program SHELXL93[40]. $R = R1$ (conventional R on the basis of observed F values with $F \geq 4\sigma(F)$), $wR = wR2$ (weighted R on the basis of F^2 values), all unique reflections used in the refinement.
[b]The reflection −10 0 4 having a negative intensity $-I \geq 3\sigma(I)$ was excluded from the refinement.
[c]Two reflections (−3 0 8 and 4 9 3) having a negative intensity $-I \geq 3\sigma(I)$ were excluded from the refinement.

TABLE II Selected bond distances (Å), bond angles (°) and torsion angels (°) for **6a**, **10f** and **12b** (e.s.d.'s in parentheses)

Bond distances		*Bond angles*		*Torsion angles*	
6a					
C1-C2	1.506(7)	S1-C1-S2	129.2(3)	S1-C1-C2-N1	−107.5(5)
C1-S1	1.729(5)	C2-C1-S1	112.1(4)	S1-C1-C2-C5	75.2(5)
C1-S2	1.589(6)	C2-C1-S2	118.6(4)	S2-C1-C2-N1	75.0(6)
C2-C5	1.461(7)	C1-C2-C5	117.2(5)	S2-C1-C2-C5	−102.3(5)
C2-N1	1.290(7)	C1-C2-N1	119.0(5)	C3-N1-C2-C1	10.8(8)
C3-N1	1.483(7)	C5-C2-N1	123.7(5)	C3-N1-C2-C5	−172.1(5)
C4-N1	1.481(7)	C2-N1-C3	123.5(5)	C4-N1-C2-C1	−169.2(5)
		C2-N1-C4	123.8(5)	C4-N1-C2-C5	7.9(8)
		C3-N1-C4	112.7(5)	N1-C2-C5-C6	52.8(8)
				N1-C2-C5-C10	−131.7(6)
				C1-C2-C5-C6	−130.0(6)
				C1-C2-C5-C10	45.4(7)
10f					
C1-C2	1.501(4)	S1-C1-S2	127.6(2)	S1-C1-C2-N1	−107.4(3)
C1-S1	1.625(3)	S1-C1-C2	119.8(2)	S2-C1-C2-N1	72.9(3)
C1-S2	1.704(3)	S2-C1-C2	112.6(2)	S1-C1-C2-C3	74.7(3)
C2-C3	1.485(4)	C1-C2-C3	117.3(2)	S2-C1-C2-C3	−105.0(3)
C2-N1	1.277(4)	C1-C2-N1	123.8(3)	C1-C2-C3-C4	28.2(4)
C9-C10	1.384(5)	C3-C2-N1	118.8(3)	N1-C2-C3-C4	−149.8(3)
C9-N1	1.423(4)	C2-N1-C9	122.5(3)	C1-C2-C3-C8	−156.6(3)
C10-C11	1.378(5)			N1-C2-C3-C8	25.3(4)
				C1-C2-N1-C9	−0.7(5)
				C3-C2-N1-C9	177.2(3)
				C2-N1-C9-C10	−115.1(4)
				C2-N1-C9-C11	70.7(4)
12b					
C1-C2	1.556(4)	S1-C1-S2	123.9(2)	C2-C1-S2-C17	174.0(2)
C1-S1	1.636(3)	S1-C1-C2	121.8(2)	S1-C1-S2-C17	2.5(3)
C1-S2	1.736(3)	S2-C1-C2	113.7(2)	C1-C2-N1-C9	70.8(3)
C2-C3	1.526(4)	C1-C2-C3	113.5(2)	C1-C2-N1-C12	−163.1(2)
C2-N1	1.486(4)	C1-C2-N1	108.7(2)	C3-C2-N1-C9	−53.5(3)
C2-N2	1.473(4)	C1-C2-N2	107.4(2)	C3-C2-N1-C12	72.6(3)
C17-S2	1.795(3)	C3-C2-N1	109.1(2)	N2-C2-N1-C9	−173.7(2)
		C3-C2-N2	111.1(2)	N2-C2-N1-C12	−47.6(3)
		N1-C2-N2	106.8(2)	C1-C2-N2-C13	−72.0(3)
		C2-N1-C9	115.5(2)	C1-C2-N2-C16	59.8(3)
		C2-N1-C12	116.3(2)	C3-C2-N2-C13	52.6(3)
		C9-N1-C12	106.6(2)	C3-C2-N2-C16	−175.5(3)
		C2-N2-C13	117.8(2)	N1-C2-N2-C13	171.5(2)
		C2-N2-C16	117.2(2)	N1-C2-N2-C16	−56.6(3)
		C13-N2-C16	108.2(2)		
		C1-S2-C17	102.9(2)		

grease. All intensity measurements have been performed at room temperature on a Stoe STADI4 diffractometer using MoK_α-radiation (λ = 0.71073 Å, graphite monochromator). Lp correction has been applied for the intensity data of **6a**, **10f** and **12b**. An absorption correction has been applied only for **6a** (Psi-scans on 12 reflections, max. and min transmission factors: 0.521 and 0.423, respectively).

Structures were solved by direct methods using the program SHELXS86[39]. The full-matrix least-squares refinement was based on F values in the case of **6a** (program SHELX76[40]) and on F^2 values for compounds **10f** and **12b** (program SHELXL93[38]). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of compounds **6a** and **12b** are placed in positions calculated for geometrical reasons while those of **10f** were located in a difference Fourier and refined isotropically. Crystal data and some relevant details concerning the intensity measurement and structure refinement of compounds **6a**, **10f** and **12b**, respectively, are given in Table I. Structural diagrams have been done using the ORTEPII[41] program with the thermal ellipsoids drawn at the 50% level. Further details of the X-ray crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany referring to the no.'s CSD-400456 (**6a**), CSD-400458 (**10f**) and CSD-401406 (**12b**), respectively, names of the authors and citation of the paper. In Table II selected bond distances, bond angles and torsion angles for the three investigated compounds are summarized.

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