α-Thioxothioamides: A Formal [4+1] Cycloaddition Reaction with Isocyanides and Diisocyanides and its Application to a New Straightforward Formation of Extended Tetrathiafulvalenes

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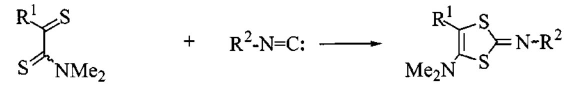
A number of 2-(alkylimino) and 2-(arylimino)-1,3-dithioles (aza DTFs) bearing push-pull substituents have been prepared under mild conditions according to the title procedure. This novel strategy relies upon the fact that the use of conjugated diisocyanides allows an effective synthesis of new extended tetrathiafulvalenes (TTFs). The two dithiole moieties are linked by a conjugated framework that incorporates a phenyl, biphenyl or azobiphenyl group. High and low temperature measurements are required in order to understand the complex ^1H and ^{13}C NMR spectra of the prepared mono-, bis- and tris-(1,3-dithiole) derivatives. Their electrochemical oxidations are also described.

Introduction

Since their early development,[1] the α-thioxothioamides **1** have been the subject of two recent preparative and mechanistic studies[2] and the factors governing the facility and regioselectivity of their [4 + 2] cycloaddition reactions are now well established. To date, however, the conjugated heterodienes **1** have not been involved in a [4 + 1] cycloaddition process.

As part of our continuing investigation of the chemistry of isocyanides and especially their formal [1 + 4] cycloadditions with conjugated aza,[3] diaza[4] and azathiadienes,[5] we became interested in examining the possibility of cyclizing the 1,4-dithiabutadiene system **1** under similar conditions. If successful, this reaction could provide a useful and straightforward route to 6-aza-1,3-dithiafulvenes (aza DTFs **2**, Scheme 1). Moreover, suitable diisocyanides make the α-thioxothioamides **1** attractive starting materials for the design of new extended tetrathiafulvalene derivatives (TTFs) that bear push-pull substituents. A literature survey revealed that this type of procedure is confined to dimethyl tetrathiooxalate ($Me_2C_2S_4$) and standard monoisocyanides.[6]

The generation of functionalized 2-imino-1,3-dithioles (aza DTFs) has received recurrent attention in recent years owing to their obvious application as organic conducting materials.[7,8] The main synthetic approaches are based on the condensation of 1,3-dithiolium cations with appropriate primary amines[7−9] and the alkylation of dithiocarbamate salts by α-haloketones[10] or counterparts.[11] Another synthetic route involves treating 4,5-dihydro-5-thioxo-1,3,4-thiadiazoles[12] or 3-thioxo-1,2,4-dithiazoles[13] with a range of alkynes in a [3+2] cycloaddition process. Alternative methods used for the synthesis of these dithiole derivatives include the thermal decomposition of 1,3-dithiol-2-yl azides,[9a,14] the bromination of *S*-(pyrrolyl)dithiocarbamates,[15] the addition of thioacids to 2-chloro-3-thiocyanatopyridine[16] and the reaction of a 2,2-dichloro-1,3-dithiole with primary amines.[17] In recent research in our laboratory, new examples have been developed in connection with their electrochemical redox[8a] and non-linear optical properties[8a,11] as well as their potential as modified TTFs that include a *p*-diaminophenyl group in the conjugated spacer chain.[8b,8c]



1

2

1	R^1
a	Ph
b	2-thienyl
c	4-ClC_6H_4
d	4-$NO_2C_6H_4$
e	4-$MeOC_6H_4$
f	*t*-Bu

2	R^1	R^2
a	Ph	*t*-Bu
b	Ph	*i*-Pr
c	2-thienyl	*t*-Bu
d	4-ClC_6H_4	*t*-Bu
e	4-$NO_2C_6H_4$	*t*-Bu
f	4-$NO_2C_6H_4$	*i*-Pr
g	4-$NO_2C_6H_4$	CH_2Tos
h	4-$NO_2C_6H_4$	2,6-$Me_2C_6H_3$
i	4-$NO_2C_6H_4$	4-$Me_2NC_6H_4$
j	4-$NO_2C_6H_4$	4-(4-$NH_2C_6H_4CH_2$)C_6H_4

Scheme 1. New route to aza DTFs

The purpose of the present paper is to develop the scope of the novel method depicted in Scheme 1 and to report on its application to bis- and tris-(1,3-dithiole) derivatives through a one-step procedure. We have also considered the electrochemical oxidation behaviour of some of the aza DTFs **2** and extended TTFs. The formation and trapping of $Me_2C_2S_4$ were also briefly described to give a similar aza DTF.

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Results and Discussion

Reactions of α-Thioxothioamides 1 and $Me_2C_2S_4$ with Monoisocyanides

A variety of thioamides **1** and representative isocyanides have been used to afford the corresponding aza DTFs **2** in good to excellent yields (see Scheme 1 and Table 1). The reactions were performed in refluxing CH_3CN (method A) or CH_2Cl_2 at room temperature (method B). The reactions were clearly accelerated by the introduction of an electron-withdrawing group onto the aromatic substituent R^1. Thus, the component **1d** underwent fast cycloadditions under surprisingly mild conditions with almost all of the isocyanides, whereas the reactivity of the dienes **1a,b** was widely attenuated (for example, compare entries 1 and 3 with entry 5). Owing to the presence of an electron-releasing substituent R^1, the thioamides **1e,f** did not give any reaction with *tert*-butyl isocyanide. The starting products **1** were recovered fully even after a prolonged heating at reflux in CH_3CN (ten days or more). Note that the C-4 of the molecules **2e−j** bears a good donor group while C-5 bears an acceptor, such conjugated substituents giving rise to a push-pull effect of potential interest for nonlinear optical applications.[8a,11]

Table 1. Reactions of α-thioxothioamides **1** with monoisocyanides[a]

Entry	Thioamide	Isocyanide (R^2)	Method	Time (h)	2-Iminodithiole[b] (yield %)
1	**1a**	*t*Bu	A	48	**2a** (68)
2	**1a**	*i*Pr	A	72	**2b** (69)
3	**1b**	*t*Bu	A	120	**2c** (57)
4	**1c**	*t*Bu	A	15	**2d** (75)
5	**1d**	*t*Bu	A	0.5	**2e** (84)
6	**1d**	*t*Bu	B	2	**2e** (82)
7	**1d**	*i*Pr	B	5	**2f** (90)
8	**1d**	CH_2Tos	B	60	**2g** (57)
9	**1d**	2,6-$Me_2C_6H_3$	B	5	**2h** (80)
10	**1d**	4-$Me_2NC_6H_4$	B	5	**2i** (90)
11	**1d**	4-XC_6H_4[c]	B	5	**2j** (61)

[a] The reactions were performed with a 1 M solution of thioamide, either in refluxing MeCN (method A) or in CH_2Cl_2 at room temp. (method B) and with a large excess of isocyanide (2 equiv., except for entries 8 and 11:1.5 equiv.). The specified times were required for the full conversion of the starting thioamides and the progress of the reaction was monitored by ^1H NMR spectroscopy. − [b] Purified products yields after flash chromatography and/or crystallization. − [c] X = 4-$NH_2C_6H_4CH_2$.

The structures of the compounds **2a-j** were assigned on the basis of the NMR spectroscopic data and were confirmed by high-resolution mass-spectral studies or satisfactory elemental analyses. All of the aza DTFs **2** were obtained as mixtures of *syn* and *anti* geometrical isomers with respect to the exocyclic C−N double bond (ratio about 50:50). Thus, the ^1H and ^{13}C NMR spectra exhibit two series of signals at room temperature (cf. Table 2 and Experimental Section). A higher temperature measurement (60 °C) reveals only one series of resonances for **2e** according to the average of the corresponding signals, which suggests a rapid *syn-anti* isomerization.

Although this type of heterocyclization can be classified as a [4 + 1] cycloaddition reaction, it probably proceeds stepwise via a transient zwitterionic nitrilium intermediate and a spontaneous ring-closure second step according to a previously assumed process.[6] The mechanism illustrated by Scheme 2 is consistent with the accelerative effect of an electron-attracting group R^1.

The electrochemical reduction of carbon disulfide has been studied by several research groups and a variety of products or intermediates have been reported.[18,19] However, the stoichiometry in Scheme 3 can be realized under accurate conditions, in order to avoid further reduction[20] to trithiocarbonate (CS_3^{2-}) and 1,3-dithiole-2-thione-4,5-dithiolate ($C_3S_5^{2-}$, DMIT). Thus, the tetrathioxalate **3** ($C_2S_4^{2-}$) was obtained in large quantities by reduction of CS_2 at a mercury-pool cathode (−1.5 V vs. Ag/AgCl) in acetonitrile solution saturated with NEt_4Br.[18,21] Treatment of the dianion **3** with methyl iodide was shown to furnish a great number of alkylated sulfur derivatives besides the $Me_2C_2S_4$ **4**.[22] Surprisingly, we have found that the methylation of **3** at low temperature, in the presence of *tert*-butyl isocyanide as the trapping reagent, produces the bis(methylthio)-2-imino-1,3-dithiole **5** in a satisfactory yield (Scheme 3). Such an approach opens an unprecedented route from CS_2 to new aza DTFs substituted by two alkylthio groups that are not easily accessible by other methods.[6]

The stability of aza DTFs lies within the nature of the substituents. The dithioles 2**a,b** were slowly hydrolyzed upon exposure to atmospheric moisture at room temperature. This reaction results in a ring-opening to give the dithiocarbamates **6a,b** (Figure 1). In contrast, the other cycloadducts **2** and **5** can be stored for several weeks without any alteration.

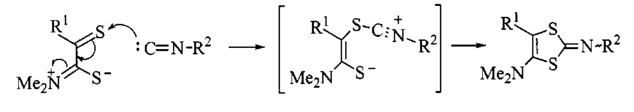
Reaction of α-Thioxothioamide 1d with Di and Triisocyanides

The efficiency of the dithiabutadiene **1d**, which bears a 4-nitrophenyl group, to incorporate diverse isocyanides encouraged us to explore its behaviour in the presence of the bi and tridentate species **7** and **8** as shown in Figures 2 and 3. Representative results of this investigation are summarized in Table 3. Two compounds could be isolated from the 4,4′-diisocyanodiphenylmethane **7a**, in yields which were highly dependent upon the excess of this reagent. The use of **7a** in a twofold excess resulted in the formation of the 1:1 adduct **9** as the major product and the 1:2 adduct **10a** in only poor yield (entry 1). The formation of **10a** as the major product was favoured by the use of a large excess of the thioxothioamide **1d** (entry 2). In other cases, the reactions proceeded smoothly at room temperature with stoichiometric quantities of diisocyanides **7b−g** (or slight excess) to give the *N,N*′-bis[1,3-dithiol]-2-ylidene diamino derivatives **10b−g** in nearly quantitative yields. The 1,2-diisocyanobenzene **7e** proved only to be rather unstable and difficult to handle and we have less satisfactory yields for **10e** than for **10d** (cf. the entries 6 and 7). Similarly, difficulties were encountered in the purification of the tricycloadduct **11** as a result of which the yield in Table 3 is lowered (entry 5). The use of ethylene tetrathiolate **3** in the presence of

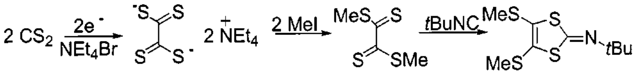
Table 2. NMR chemical shifts and multiplicities for main carbon atoms of aza DTFS **2**, **9**[a][b]

	C−2	C−4	C−5 (^3J = 3.8−4.2)	$N(CH_3)_2$ (^1J = 136)	=N−C[c]	C_{arom}[d] (^3J = 7.9−8.3)
2a	152.1, 153.1 (s)	140.0, 140.4 (m)	119.1, 120.7 (t)	44.6, 44.7 (qq)	57.5, 57.6 (m)	131.8, 132.7 (t)
2b	156.5, 156.9 (d, ^3J = 9.8)	139.8, 139.9 (m)	118.4, 120.1 (t)	44.7 (qq)	58.2, 59.8 (dm, ^1J = 131)	132.1, 132.8 (t)
2c	150.1, 150.7 (s)	138.1, 138.5 (m)	118.2, 118.7 (br)	43.1, 43.4 (qq)	56.8, 56.9 (m)	131.8, 132.4 (m)
2d	150.2, 151.2 (s)	139.9, 140.2 (m)	116.6, 118.2 (t)	43.6, 43.7 (qq)	56.6, 56.7 (m)	129.3, 130.2 (t)
2e	150.2, 151.2 (s)	145.2, 145.4 (m)	114.7, 116.8 (t)	45.0, 45.2 (qq)	53.8, 58.4 (m)	139.1, 140.0 (t)
2f	154.0, 153.4 (d, ^3J = 9.8)	143.1, 143.7 (m)	112.4, 114.5 (t)	43.6, 43.7 (qq)	57.5, 59.1 (dm, ^1J = 131)	137.8, 138.5 (t)
2g	167.5, 167.6 (t, ^3J = 8.7)	144.1, 145.6 (m)	112.7, 116.5 (t)	44.7 (qq)	76.3, 77.5 (t, ^1J = 146)	138.1, 138.7 (t)
2h	160.8 (br)	145.2 (m)	115.3 (br)	45.1 (qq)	149.5 (br)	139.4 (br)
2i	156.5, 157.1 (s)	144.3, 147.7 (m)	113.6, 115.3 (t)	40.7, 44.6, 44.7 (qq)	140.1, 140.8 (t, ^3J = 8.4)	138.7, 139.4 (t)
2j[e]	159.9, 160.5 (s)	144.4, 144.9 (m)	113.8, 115.5 (t)	44.7, 44.9 (qq)	148.6, 149.2 (t, ^3J = 8.7)	138.7, 139.2 (t)
9[f]	160.6, 161.2 (s)	154.6, 155.2 (m)	114.0, 115.8 (t)	45.0, 45.1 (qq)	149.4, 150.1 (t,^3J = 8.9)	138.9, 139.5 (t)

[a] δ (ppm) and J (Hz) in $CDCl_3$ solutions at 50.3 MHz except for **2a,b,j** (75.5 MHz). − [b] The endocyclic carbon atoms are numbered in such a way that the dimethylamino group is at C-4. − [c] Exocyclic carbon on the imino nitrogen atom. − [d] Quaternary carbon atom of the aromatic on the 5 position. − [e] Other selected value: δ = 40.7 (tm, ^1J = 127 Hz). − [f] Other selected values: δ = 48.7 (tm, ^1J = 127 Hz), 171.4 (br).



Scheme 2. Postulated mechanism for the formation of aza DTFs



Scheme 3. Formation and trapping of dimethyl tetrathiooxalate

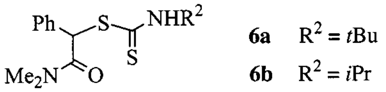


Figure 1. Hydrolysis products

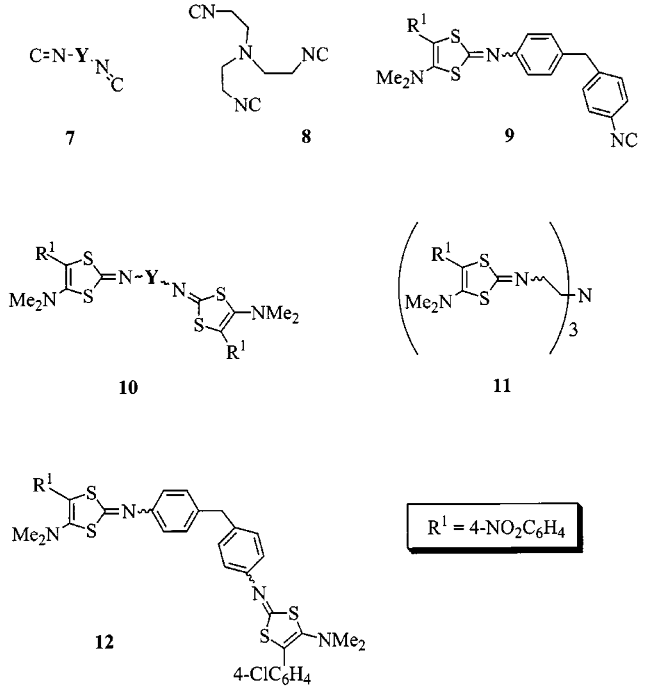


Figure 2. Polyisocyanides, poly-(aza DTFs) and extended TTFs

MeI and diisocyanide **7a** or **7e**, as described above for *tert*-butyl isocyanide, generated only an intractable mixture of several products.

We especially emphasize the value of using the conjugated diisocyanides **7d−g**. The reactions provide a convenient one-step synthesis of new symmetrical, highly conjugated bis(1,3-dithiole) compounds **10d−g** (Table 3, entries 6−9). The two push-pull polarized heterocycles are attached through the imines nitrogen's by a chain that incorporates a phenyl, biphenyl or azobiphenyl moiety. Products **10d−g** can be viewed as azavinylogues of the TTF derivatives. Only a few examples of similar imino extended TTFs have been reported in the literature.[8b,8c,17]

NMR studies allow some consideration regarding the number and nature of isomers for the bis(1,3-dithiole) derivatives **10**. Theoretically, the double cycloaddition can produce three isomeric species corresponding to the possible (E) and (Z) configurations of the two exocyclic C=N bonds. Such isomers: (EE), (ZZ) and (EZ) equivalent to (ZE) might be found in the statistical ratio 25:25:50. Thus, four series of signals might be observed for the dithiole end-groups with nearly equal intensities.

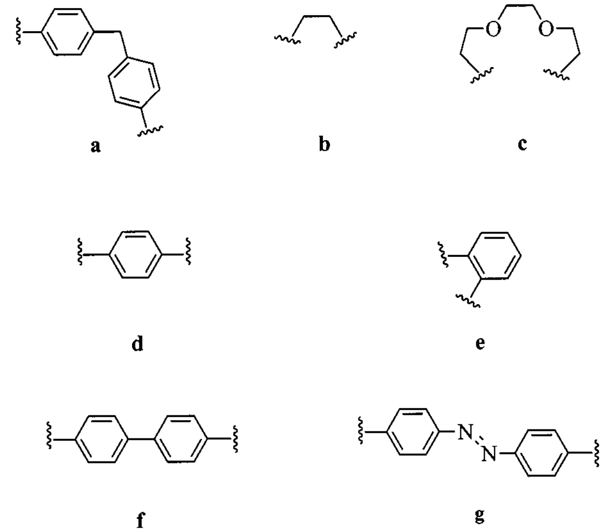


Figure 3. Structures **a−g** for the linking group **Y**

Generally, the ^{1}H and ^{13}C NMR spectra of the compounds **10** exhibited only two sets of slightly broad signals of the same intensities at room temperature. This is in accordance with the presence of (*E*) and (*Z*) species for one dithiole moiety (cf. Table 4 and Experimental Section). No significant difference was found between the isomer (*EE*) and part (*E*) of (*EZ*) and between the isomer (*ZZ*) and part (*Z*) of (*EZ*). High and low temperature measurements showed important spectral modifications. Between 55 °C and 75 °C, a single series of signals was observed for all of the extended TTFs **10d−g**, which is due to a fast (*E*)-(*Z*) isomerization. At low temperatures (−10 °C or −55 °C), this equilibrium became slow and four series of well-resolved protons signals were observed (see the Experimental Section). Similar evidence for the formation of three isomers was found in the case of **10b** at −10 °C.

Table 3. Reactions of the α-thioxothioamide **1d** with di and triisocyanides[a]

Entry	Isocyanide	Isocyanide/**1d**	Time[b] (h)	Products (yield %)[c]
1	**7a**	2	5	**9** (46); **10a** (28)
2	**7a**	0.6	8	**9** (14); **10a** (61)
3	**7b**	0.6	15	**10b** (85)
4	**7c**	0.6	7	**10c** (76)
5	**8**	0.34	10	**11** (60)
6	**7d**	0.52	15	**10d** (82)
7	**7e**	0.6	15	**10e** (70)
8	**7f**	0.55	15	**10f** (80)
9	**7g**	0.6	15	**10g** (79)

[a] The reactions were performed at room temp., starting from a 1 M solution of thioamide **1d** in CH_2Cl_2 (method B). − [b] Times required for the complete conversion of the starting material **1d**. − [c] Yields represent isolated and purified products after flash chromatography or crystallization.

Preparation of Unsymmetrical Bis(1,3-dithiole) Derivatives

Considering the possibility of obtaining the highly functionalized monocycloadducts **2j** and **9** in adequate yields, we thought that it would be interesting to extend the scope of our method by using them as starting materials in similar reactions. The isocyanide **9** was treated with a twofold excess of the thioxothioamide **1c** to give the compound **12** in 47% yield (method A). According to a known procedure,[8b] the reaction of the amine **2j** with a 2-piperidino-1,3-dithiolium salt resulted in the preparation of another unsymmetrical molecule **13** (Scheme 4).

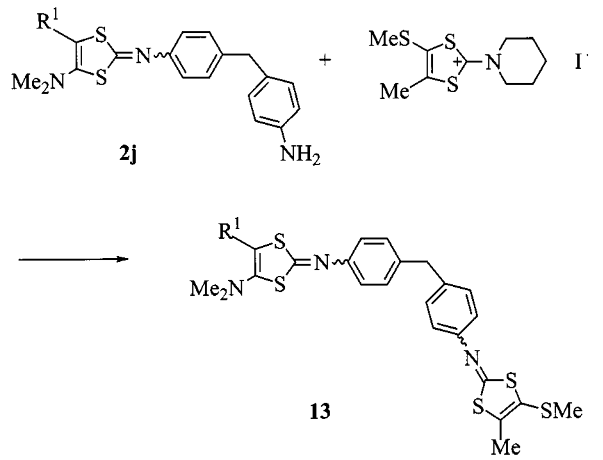
Electrochemical Oxidation Behaviour

Some of the compounds (**2** and **10)** were examined by cyclic voltammetry (CV). Measurements were carried out in CH_2Cl_2 or CH_3CN solutions in order to achieve the greatest solubility of the substrates (Table 5). Imino extended

Table 4. NMR chemical shifts and multiplicities for main carbon atoms of bis- and tris-(1,3-dithiole) derivatives **10−12**[a][b]

	C−2	C−4	C−5 (^3J = 4.2−4.5)	$N(CH_3)_2$ (^1J = 136)	=N−C[c]	C_{arom}[d] (^3J = 8−8.4)
10a[e]	160.3, 160.9 (s)	145.2, 145.6 (m)	114.2, 116.1 (t)	45.1, 45.2 (qq)	149.2, 149.8 (t, ^3J = 9)	139.0, 139.6 (t)
10b	159.2, 159.3, 159.7, 159.8, (t, ^3J = 8.5)	144.7, 144.8, 145.7, 145.8 (m)	114.0, 114.1, 116.7, 116.8 (t)	45.1, 45.2 (qq)	57.1, 58.5, 58.6 (tt, ^1J = 136, ^3J = 4)	139.1, 139.7 (t)
10c[f]	158.4, 158.8 (t, ^3J = 8)	144.2, 145.3 (m)	113.5, 116.3 (t)	44.7, 44.8 (qq)	56.5, 58.0 (t, br, ^1J = 133)	138.7, 139.4 (t)
10e	161.4, 161.9 (s)	144.7, 145.0 (m)	114.2, 115.8 (br)	44.7 (qq)	142.2, 142.7 (m)	138.7, 139.2 (m)
10e[g]	161.1 (s)	144.7 (m)	115.5 (br)	44.6 (qq)	142.4 (m)	139.0 (m)
10f	160.4, 161.0 (s)	144.3, 144.9 (m)	114.0, 115.9 (t)	44.7, 44.8 (qq)	149.8, 150.5 (t, ^3J = 8.3)	138.6, 139.1 (t)
10g	161.5, 161.8 (br)	144.0, 145.0 (m)	114.0, 115.9 (br)	44.8 (qq)	152.9, 153.5 (br)	138.4, 139.0 (br)
10g[h]	163.1, 163.5 (s)	145.0, 145.5 (m)	112.9, 115.3 (t)	45.2, 45.3 (qq)	153.1, 153.8 (t, ^3J = 8.3)	138.6, 139.2 (t)
11[i]	157.6, 158.0 (br)	144.3, 145.2 (m)	113.8, 116.3 (br)	44.8 (qq)	55.6, 57.0 (t, ^1J = 133)	138.7, 139.4 (t)
12[j]	159.8, 160.4, 161.3, 161.9 (s)	146.1, 146.4 (m)	114.0, 115.8, 117.3, 119.0 (t)	44.6, 44.7, 44.8 (qq)	148.7, 149.0, 149.4, 149.6 (t, ^3J = 8.1)	130.3, 130.9 (screened) 138.6, 139.2 (t)

[a] δ (ppm) and *J* (Hz) in $CDCl_3$ solutions at 50.3 MHz except for **10e−g, 11, 12** (75.5 MHz). − [b] The endocyclic carbon atoms are numbered in such a way that the dimethylamino group is at C-4. − [c] Exocyclic carbon on the imino nitrogen atom. − [d] Quaternary carbon atom of the aromatic on the 5 position. − [e] Other selected value: δ = 41.4 (tm, ^1J = 127 Hz). − [f] Other selected values: δ = 70.6, 70.7 (t, br, ^1J = 140 Hz). − [g] At 55 °C. − [h] At −55 °C. − [i] Other selected values: δ = 54.5, 54.6 (t, br, ^1J = 133 Hz). − [j] Other selected value: δ = 41.0 (tm, ^1J = 131 Hz).



Scheme 4. Another preparation of a bis(1,3-dithiole) derivative

TTFs **10e,g** display a single, quasi-reversible system, which is similar to a two-electron transfer ($\Delta E = 0.05$ V), as previously reported for structurally related compounds.[8b] In the cases of other studied aza DTFs and TTFs, the number of electrons involved in the process is difficult to assess owing to the higher values of ΔE (≥ 0.06 V). The first of the two reversible waves, which was observed in the cyclic voltammogram of **2i**, presumably reflects the oxidation of the aromatic substituent R^2 (4-dimethylaminophenyl group).

Table 5. Cyclic voltammetry data for some aza DTFs **2**, bis(1,3-dithiole) derivative **10a** and imino extended TTFs **10d–g**

Compound	E_{anodic}	$E_{cathodic}$	ΔE
2g[a]	0.93	0.86	0.07
2h[a]	0.86	0.80	0.06
2i[a]	0.66	0.60	0.06
	0.78	0.72	0.06
10a[b]	0.82	0.76	0.06
10d[b]	0.93	0.85	0.08
10e[b]	0.85	0.80	0.05
10f[b]	0.93	0.86	0.07
10g[b]	0.88	0.83	0.05

[a] TBAPF$_6$ 0.5 mol L^{-1} in acetonitrile; 0.1 v s^{-1}; V vs. SCE. – [b] TBAPF$_6$ 0.5 mol L^{-1} in dichloromethane; 0.1 v s^{-1}; V vs. SCE.

Conclusion

The formal [1+4] cycloaddition reaction of the dithiabutadienes with the isocyanides is a conceptually simple and direct method for the preparation of aza DTFs. We have described the use of this method for the generation of the dithioles **2** and **5**, which are not readily accessible by standard procedures. An efficient synthetic strategy for linking several rings by aliphatic or aromatic groups was also developed and bis-, as well as, tris-(dithiole) species and imino extended TTFs were obtained under mild conditions. All of these results further increase the potential of the starting α-thioxothioamides **1,** which are useful as building blocks in heterocyclic chemistry.

Experimental Section

General: NMR: Bruker ARX 200 spectrometer (200 MHz for ^{1}H and 50.3 MHz for ^{13}C) or Bruker AM 300 WB spectrometer (300 MHz for ^{1}H and 75.5 MHz for ^{13}C) in $CDCl_3$ (internal standard Me_4Si) at room temperature unless otherwise indicated. – HMRS: Centre Régional de Mesures Physiques de l'Ouest; Varian Mat 311 spectrometer, EI mode using a potential of 70 eV for compounds **2**, **6**, **9**; MS/MS ZabSpec TOF Micromass spectrometer, ionization mode positive LSIMS with CS^+, matrix *m* NBA for compounds **10–13**. – IR: Perkin–Elmer 1420 spectrophotometer; suspensions in nujol. – Elemental analyses: Analytical laboratory CNRS.

CV measurements were performed with a Princeton Applied Research 362 potentiostat, using Pt working and counter electrodes, and saturated calomel electrode (SCE) as a reference. The experiments were carried out under nitrogen, in CH_2Cl_2 or CH_3CN, with Bu_4NPF_6 as the supporting electrolyte (0.5 mol L^{-1}). The scan rate was 0.1 V s^{-1}.

Starting Materials: The α-thioxothioamides **1** were readily available from the corresponding ketones $R^1C(O)CH_3$ by a previously reported three-step procedure.[1,2]

Toluene-4-sulfonylmethyl isocyanide and 2,6-dimethylphenyl isocyanide were purchased from Fluka. Other monoisocyanides were synthesized according to the well-known Hofmann carbylamine reaction: treatment of the primary amines with chloroform in CH_2Cl_2/aqueous NaOH system, in the presence of benzyltriethylammonium chloride as phase-transfer catalyst.[23] *tert*-Butyl isocyanide,[24] isopropyl isocyanide[24] and 4-(dimethylamino)phenyl isocyanide[25] were obtained in excellent yields. The crude product from 4,4′-methylenedianiline (9.9 g, 50 mmol) was a mixture of the diisocyanide **7a** (3.8 g, 35% yield) and the monoisocyanide (see below) which were separated by flash chromatography on a Merck 90 alumina column with CH_2Cl_2/hexane (1:1) and then CH_2Cl_2 as the eluents.

The polyisocyanides, except **7c**, have already been described in the literature, for example in the following principal references: 4,4′-diisocyanodiphenylmethane (**7a**);[26,27] 1,2-diisocyanoethane (**7b**);[28,29] 1,4-diisocyanobenzene (**7d**);[26] 1,2-diisocyanobenzene (**7e**);[30] 4,4′-diisocyanobiphenyl (**7f**);[26,31] 4,4′-diisocyanoazodiphenyl (**7g**);[27] tris(2-isocyanoethyl)amine (**8**).[29] The 1,2-phenylenediisocyanide **7e** is a rather unstable compound that turns brown at room temperature and decomposes within a few hours to give mainly polymeric material. The diisocyanide **7c** was conveniently prepared from 2,2′-(ethylenedioxy)bis(ethylamine) (14.8 g, 100 mmol) by the customary phase-transfer procedure[23] and isolated by flash chromatography on alumina with CH_2Cl_2/Et_2O (1:1) as the eluent.

The orange-coloured ethylene tetrathiolate **3** was accessible and purified as described in the review by Jeroschewski.[18] – $^{13}C\{^1H\}$ NMR (H_2O/D_2O, 75.5 MHz): $\delta = 9.4$ (s), 54.7 (t, $^1J_{CN} = 2.9$ Hz), 270.2 (s).

4-Amino-4′-isocyanodiphenylmethane: M.p. 105 °C (CH_2Cl_2/hexane) (2.6 g, 25% yield). – IR: $\tilde{\nu} = 3400$ cm^{-1}, 3320 (NH), 2140 (N=C). – ^{1}H NMR (300 MHz): $\delta = 3.60$ (br, 2 H), 3.85 (s, 2 H), 6.61, 6.92, 7.15, 7.23 (4 d, $J = 8.4$ Hz, 8 H). – ^{13}C NMR (75.5 MHz): $\delta = 40.7$ (tm, $^1J = 127$ Hz), 115.2, 115.3, 126.3, 129.5 (4 nonquat. arom. C), 129.7, 129.8, 143.8 (3 m), 144.9 (t, $^3J = 8.5$ Hz), 163.4 (br). – $C_{14}H_{12}N_2$ (208.26): calcd. C 80.74, H 5.81, N 13.45; found C 80.51, H 5.63, N 13.39.

3,6-Dioxaoctane-1,8-diisocyanide (7c): B.p. 150 °C/0.045 Torr (Büchi kugelrohr apparatus) (6.05 g, 36% yield). − IR: $\tilde{\nu}$ = 2133 cm^{-1} (N=C). − ^{1}H NMR (200 MHz): δ = 3.59 (m, 4 H), 3.71 (m, 4 H), 3.72 (s, 4 H). − ^{13}C NMR (50.3 MHz): δ = 42.3 (tt, ^1J = 145 Hz, $^1J_{CN}$ = 7 Hz), 69.0 (tm, ^1J = 145 Hz), 71.1 (tt, ^1J = 142 Hz, ^3J = 2.7 Hz), 157.5 (t, br, $^1J_{CN}$ = 5.4 Hz). − $C_8H_{12}N_2O_2$ (168.20): calcd. C 57.13, H 7.19, N 16.66; found C 56.95, H 7.07, N 16.55.

The Reaction of α-Thioxothioamides with Mono- and Polyisocyanides. − General Procedure: A suspension of the thioamide **1** (5 mmol) and the appropriate isocyanide was prepared in 5 mL of dry MeCN (method A) or CH_2Cl_2 (method B). The excess of the isocyanide used, the operating temperature and the reaction time are indicated in Table 1 and 3. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. A few of the cycloadducts (**2i**, **10b**, **10d**, **10f**, **10g**) precipitated as highly coloured solids from the reaction medium. They were collected by filtration. Otherwise, the solvent was removed under reduced pressure and the residual syrup was triturated with MeOH to give the crystalline materials **2d−f** and **10c**. In other cases, the iminodithioles were isolated and then purified by flash chromatography on silica gel using diverse eluents: petroleum ether/diethyl ether (2:1) for **2a−c**; CH_2 Cl_2 then Et_2O for **2g,j** and **10e**; CH_2Cl_2/hexane (2:1) for **2h**; CH_2Cl_2 then MeOH for **11**. The mixture obtained from the diisocyanide **7a** (Table 3, entries 1,2) was treated under similar conditions. The SiO_2 column was first eluted with CH_2Cl_2 to collect the monocycloadduct **9** and then eluted with Et_2O to give the bis(1,3-dithiole) **10a**. − Yields and selected ^{13}C NMR spectroscopic data: see Table 1−4.

***tert*-Butyl-*N*-[4-(Dimethylamino)-5-phenyl-1,3-dithiol-2-ylidene]amine (2a):** 0.99 g, 3.4 mmol. − M.p. 58 °C (petroleum ether). − ^{1}H NMR (300 MHz) : δ = 1.34, 1.35 (2 s, 9 H), 2.55 (s, 6 H), 7.23−7.55 (m, 5 H). − MS: calcd. for $C_{15}H_{20}N_2S_2$ *m/z* = 292.1068 [$M^{+\bullet}$]; found 292.1061 − $C_{15}H_{20}N_2S_2$ (292.46): calcd. C 61.60, H 6.89, N 9.58, S 21.92; found C 61.45, H 6.99, N 9.70, S 21.65.

***N*-[4-(Dimethylamino)-5-phenyl-1,3-dithiol-2-ylidene]isopropylamine (2b):** 0.96 g, 3.45 mmol. − M.p. 56 °C (petroleum ether). − ^{1}H NMR (300 MHz): δ = 1.21, 1.23 (2 d, *J* = 6.2 Hz, 6 H), 2.55, 2.57 (2 s, 6 H), 3.29 (m, 1 H), 7.23−7.54 (m, 5 H). − MS: calcd. for $C_{14}H_{18}N_2S_2$ *m/z* = 278.0911 [$M^{+\bullet}$]; found 278.0903.

***tert*-Butyl-*N*-[4-(Dimethylamino)-5-(2-thienyl)-1,3-dithiol-2-ylidene]amine (2c):** 0.85 g, 2.85 mmol. − M.p. 62 °C (petroleum ether). − ^{1}H NMR (200 MHz) : δ = 1.26 1.28 (2 s, 9 H), 2.52, 2.53 (2 s, 6 H), 6.85 (m, 2 H), 7.13 (d, *J* = 3.5 Hz, 1 H). − MS: calcd. for $C_{13}H_{18}N_2S_3$ *m/z* = 298.0632 [$M^{+\bullet}$]; found 298.0627.

***tert*-Butyl-*N*-[5-(4-Chlorophenyl)-4-(dimethylamino)-1,3-dithiol-2-ylidene]amine (2d):** 1.22 g, 3.75 mmol. − M.p. 75 °C (MeOH) − ^{1}H NMR (200 MHz): δ = 1.34 (s, 9 H), 2.57 (s, 6 H), 7.29, 7.48 (2 d, *J* = 8.7 Hz, 4 H). − $C_{15}H_{19}ClN_2S_2$ (326.90): calcd. C 55.11, H 5.86, N 8.57, Cl 10.85; found C 55.14, H 5.82, N 8.60, Cl 10.88.

***tert*-Butyl-*N*-[4-(Dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]amine (2e):** 1.42 g, 4.2 mmol. − M.p. 94 °C (MeOH). − ^{1}H NMR (300 MHz): δ = 1.35 (s, 9 H), 2.64, 2.65 (2 s, 6 H), 7.69, 7.70, 8.18, 8.19 (4 d, *J* = 8.9 Hz, 4 H); at 60 °C: δ = 1.36 (s, 9H), 2.65 (s, 6 H), 7.69, 8.18 (2 d, *J* = 8.9 Hz, 4 H). − $C_{15}H_{19}N_3O_2S_2$ (337.45): calcd. C 53.39, H 5.68, N 12.45, S 19.00; found C 53.28, H 5.65, N 12.21, S 19.16.

***N*-[4-(Dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]-isopropylamine (2f):** 1.45 g, 4.5 mmol. − M.p. 95 °C (CH_2Cl_2/petroleum ether). − ^{1}H NMR (200 MHz): δ = 1.14, 1.15 (2 d, *J* = 6.2 Hz, 6 H), 2.55, 2.58 (2 s, 6 H), 3.22 (m, 1 H), 7.61, 7.63, 8.10, 8.11 (4 d, *J* = 9 Hz, 4 H). − $C_{14}H_{17}N_3O_2S_2$ (323.43): calcd. C 51.99, H 5.30, N 12.99, S 19.83; found C 52.29, H 5.19, N 13.01, S 20.03.

***N*-[4-(Dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]-tosylmethylamine (2g):** 1.28 g, 2.85 mmol. − M.p. 110 °C (CH_2Cl_2/Et_2O). − ^{1}H NMR (200 MHz): δ = 2.45 (s, 3 H), 2.62, 2.67 (2 s, 6 H), 4.59, 4.64 (2 s, 2 H), 7.37, 7.85 (2 d, *J* = 8.3 Hz, 4 H), 7.63, 7.68, 8.20, 8.21 (4 d, *J* = 9 Hz, 4 H). − MS: calcd. for $C_{19}H_{19}N_3O_4S_3$ *m/z* = 449.0538 [$M^{+\bullet}$]; found 449.0543. − $C_{19}H_{19}N_3O_4S_3$ (449.56): calcd. C 50.76, H 4.26, N 9.35; found C 50.34, H 4.24, N 8.95.

2,6-Dimethyl-*N*-[4-(dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]aniline (2h): 1.54 g, 4 mmol. − M.p. 120 °C (MeOH). − ^{1}H NMR (200 MHz): δ = 2.19 (s, 6 H), 2.58, 2.72 (br, 6 H), 7.05 (m, 3 H), 7.68, 8.19 (br, 4 H). − MS: calcd. for $C_{19}H_{19}N_3O_2S_2$ *m/z* = 385.0919 [$M^{+\bullet}$]; found 385.0932. − $C_{19}H_{19}N_3O_2S_2$ (385.50): calcd. C 59.20, H 4.97, N 10.90, S 16.63; found C 58.97, H 5.03, N 11.04, S 16.36.

4-(Dimethylamino)-*N*-[4-(dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]aniline (2i): 1.8 g, 4.5 mmol. − M.p. 165 °C (MeOH/CH_2Cl_2). − ^{1}H NMR (200 MHz): δ = 2.60, 2.69, 2.95, 2.96 (4 s, 12 H), 6.73, 6.75, 6.99, 7.01, 7.64, 7.73, 8.14, 8.19 (8 d, *J* = 8.9 Hz, 8 H). − MS: calcd. for $C_{19}H_{20}N_4O_2S_2$ *m/z* = 400.1028 [$M^{+\bullet}$]; found 400.1048. − $C_{19}H_{20}N_4O_2S_2$ (400.51): calcd. C 56.98, H 5.03, N 13.99, S 16.01; found C 57.09, H 4.99, N 14.09, S 16.48.

4-(4-Aminobenzyl)-*N*-[4-(dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]aniline (2j): 1.41 g, 3.05 mmol. − M p. 135 °C (MeOH). − ^{1}H NMR (200 MHz): δ = 2.58, 2.68 (2 s, 6 H), 3.52 (br, 2 H), 3.86 (s, 2 H), 6.61−7.21 (m, 8 H), 7.61, 7.72, 8.14, 8.20 (4 d, *J* = 8.9 Hz, 4 H). − MS: calcd. for $C_{24}H_{22}N_4O_2S_2$ *m/z* = 462.1184 [M^+]; found 462.1153. − $C_{24}H_{22}N_4O_2S_2$ (462.58): calcd. C 62.32, H 4.79, N 12.11, S 13.86; found C 62.04, H 4.90, N 12.20, S 13.90.

***N*-[4-(Dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]-4-(4-isocyanobenzyl)aniline (9):** 1.08 g, 2.3 mmol. − M.p. 128 °C (CH_2Cl_2/petroleum ether). − IR: $\tilde{\nu}$ = 2120 cm^{-1} (N=C). − ^{1}H NMR (200 MHz): δ = 2.60, 2.70 (2 s, 6 H), 3.98, 3.99 (2 s, 2 H), 6.95−7.30 (m, 8 H), 7.62, 7.73, 8.15, 8.21 (4 d, *J* = 8.9 Hz, 4 H). − MS: calcd. for $C_{25}H_{20}N_4O_2S_2$ *m/z* = 472.1026 [$M^{+\bullet}$]; found 472.1027. − $C_{25}H_{20}N_4O_2S_2$ (472.58): calcd. C 63.54, H 4.27, N 11.86, S 13.57; found C 63.14, H 4.07, N 11.82, S 13.66.

***N,N'*-Bis[4-(dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]-diphenylmethane-4,4'-diamine (10a):** 1.11 g, 1.53 mmol. − M.p. 220 °C (CH_2Cl_2/petroleum ether). − ^{1}H NMR (200 MHz): δ = 2.60, 2.70 (2 s, 12 H), 3.97 (br, 2 H), 6.98, 7.23 (2 m, 8 H), 7.63, 7.74, 8.15, 8.22 (4 d, *J* = 8.8 Hz, 8 H). − MS: calcd. for $C_{35}H_{31}N_6O_4S_4$ *m/z* = 727.1290 [M + H^+]; found 727.1288. − $C_{35}H_{30}N_6O_4S_4$ (726.90): calcd. C 57.83, H 4.16, N 11.56, O 8.80, S 17.64; found C 57.92. H 4.35, N 11.35, O 8.78, S 17.02.

***N,N'*-Bis[4-(dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]-ethane-1,2-diamine (10b):** 1.25 g, 2.12 mmol. − M.p. 201 °C (MeCN). − IR: $\tilde{\nu}$ = 1565 cm^{-1} (N=C). − ^{1}H NMR (300 MHz): δ = 2.64, 2.67 (2 s, 12 H), 3.46−3.58 (m, 4 H), 7.70, 7.72, 8.20, 8.21 (4 d, *J* = 9 Hz, 8 H); at −10 °C: δ = 2.641, 2.642 (2 s, 6 H), 2.68 (br, 6 H), 3.45−3.55 (m, 4 H), 7.70, 7.71 (2 d, *J* = 9 Hz, 2 H), 7.73, 8.21, 8.22 (3 d, *J* = 9 Hz, 6 H). − MS: calcd. for $C_{24}H_{25}N_6O_4S_4$ *m/z* = 589.0820 [M + H^+]; found 589.0824. − $C_{24}H_{24}N_6O_4S_4$ (588.73): calcd. C 48.96, H 4.11, N 14.27, S 21.78; found C 49.28, H 3.96, N 14.17, S 21.86.

***N,N′*-Bis[4-(dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]-3,6-dioxaoctane-1,8-diamine (10c):** 1.28 g, 1.9 mmol. − M.p. 160 °C (MeOH). − ^{1}H NMR (200 MHz): δ = 2.64, 2.67 (2 s, 12 H), 3.38 (m, 4 H), 3.72 (s, 4 H), 3.82 (t, J = 5.8 Hz, 4 H), 7.69, 7.72 (2 d, J = 8.6 Hz, 4 H), 8.20 (d, J = 8.5 Hz, 4 H). − MS: calcd. for $C_{28}H_{33}N_6O_6S_4$ m/z = 677.1344 [M + H$^+$]; found 677.1349. − $C_{28}H_{32}N_6O_6S_4$ (676.84): calcd. C 49.69, H 4.77, N 12.42, S 18.95; found C 49.64, H 4.84, N 12.56, S 18.91.

***N,N′*-Bis[4-(dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]-benzene-1,4-diamine (10d):** 1.30 g, 2.04 mmol. − M.p. 258 °C (CH_2Cl_2). − ^{1}H NMR (300 MHz): δ = 2.63, 2.72 (2 s, 12 H), 7.08−7.11 (br, 4 H), 7.66, 7.76, 8.19, 8.24 (4 d, J = 8.9 Hz, 8 H); at −10 °C: δ = 2.62, 2.63, 2.72, 2.73 (4 s, 12 H), 7.08, 7.10, 7.12 (3 s, 4 H), 7.67, 7.675, 7.765, 7.77, 8.185, 8.19, 8.25, 8.255 (8 d, J = 9 Hz, 8 H); at 75 °C (C_6D_6): δ = 2.07 (br, 12 H), 7.24 (s, 4 H), 7.16, 7.78 (2 d, J = 9 Hz, 8 H). − MS: calcd. for $C_{28}H_{25}N_6O_4S_4$ m/z = 637.0820 [M + H$^+$]; found 637.0824.

***N,N′*-Bis[4-(dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]-benzene-1,2-diamine (10e):** 1.11 g, 1.75 mmol. − M.p. 218 °C (acetone/CH_2Cl_2). − ^{1}H NMR (300 MHz): δ = 2.59, 2.69 (br, 12 H), 7.08 (m, 2 H), 7.19 (br, 2 H), 7.63, 7.73, 8.14, 8.20 (4 d, br, J = 7.5 Hz, 8 H); at −50 °C (CD_2Cl_2): δ = 2.51, 2.54, 2.65, 2.66 (4 s, 12 H), 7.04, 7.17 (2 m, 4 H), 7.58, 7.60, 7.715, 7.72, 8.07, 8.10, 8.16, 8.17 (8 d, J = 8.8 Hz, 8 H); at 60 °C (C_6D_6): δ = 2.02 (s, 12 H), 7.06, 7.19 (2 dd, J = 5.9 and 3.5 Hz, 4 H), 7.10 (d, br, J = 8.9 Hz, 4 H), 7.75 (d, J = 9 Hz, 4 H). − MS: calcd. for $C_{28}H_{25}N_6O_4S_4$ m/z = 637.0820 [M + H$^+$]; found 637.0826. − $C_{28}H_{24}N_6O_4S_4$ (636.78): calcd. C 52.81, H 3.80, N 13.20, S 20.14; found C 52.75, H 3.64, N 12.94, S 20.40.

***N,N′*-Bis[4-(dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]-biphenyl-4,4′-diamine (10f):** 1.42 g, 2 mmol. − M.p. 268 °C (CH_2Cl_2). − ^{1}H NMR (300 MHz): δ = 2.62, 2.72 (2 s, 12 H), 7.12, 7.65 (2 m, 8 H), 7.66, 7.76, 8.17, 8.24 (4 d, J = 8.9 Hz, 8 H); at −10 °C: δ = 2.62, 2.625, 2.73, 2.735 (4 s, 12 H), 7.13, 7.65 (2 m, 8 H), 7.665, 7.67, 7.77, 7.775, 8.175, 8.18, 8.25, 8.255 (8 d, J = 9 Hz, 8 H); at 75 °C (C_6D_6): δ = 2.09 (s, 12 H), 7.16, 7.79 (2 d, J = 9 Hz, 8 H), 7.21, 7.53 (2 d, J = 8.8 Hz, 8 H). − MS: calcd. for $C_{34}H_{29}N_6O_4S_4$ m/z = 713.1133 [M + H$^+$]; found 713.1136. − $C_{34}H_{28}N_6O_4S_4$ (712.87): calcd. C 57.29, H 3.96, N 11.79, S 17.99; found C 56.73, H 3.97, N 11.76, S 17.95.

***N,N′*-Bis[4-(dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]-azobenzene-4,4′-diamine (10g):** 1.46 g, 1.97 mmol. − M.p. 269 °C (toluene). − ^{1}H NMR (300 MHz): δ = 2.62, 2.73 (br, 12 H), 7.18, 7.97 (2 d, J = 8.7 Hz, 8 H), 7.65, 7.75, 8.18, 8.25 (4 d, br, J = 8.7 Hz, 8 H); at −55 °C: δ = 2.63, 2.76 (2 s, 12 H), 7.20, 7.97 (2 m, 8 H), 7.67, 7.79, 8.20, 8.27 (4 d, J = 9 Hz, 8 H); at 57 °C: δ = 2.68 (br, 12 H), 7.19, 7.97 (2 d, J = 8.7 Hz, 8 H), 7.70, 8.21 (2 d, br, J = 8.7 Hz, 8 H). − MS: calcd. for $C_{34}H_{29}N_8O_4S_4$ m/z = 741.1195 [M + H$^+$]; found 741.1200. − $C_{34}H_{28}N_8O_4S_4$ (740.89): calcd. C 55.12, H 3.81, N 15.12, S 17.31; found C 55.23, H 3.79, N 14.75, S 17.42.

Tris-(2-aminoethyl)-*N,N′,N′′*-tris-[4-(dimethylamino)-5-(4-nitrophenyl)-1,3-dithiol-2-ylidene]amine (11): Amorphous hemisolid (0.94 g, 1 mmol.) − ^{1}H NMR (300 MHz): δ = 2.61, 2.62, 2.64, 2.66, 2.67, 2.68 (6 s, 18 H), 3.05, 3.37 (2 m, 12 H), 7.66−7.72 (m, 6 H), 8.14−8.21 (m, 6 H). − MS: calcd. for $C_{39}H_{43}N_{10}O_6S_6$ m/z = 939.1691 [M + H$^+$]; found 939.1729.

Preparation of the Unsymmetrical Bis(1,3-dithiole) Derivatives: A mixture of α-thioxothioamide **1c** (0.97 g, 4 mmol) and isocyanide **9** (0.88 g, 1.86 mmol) in anhydrous MeCN (10 mL) was refluxed for 70 h. Concentration of the crude solution left a reddish residue, which was purified by flash-chromatography on Merck silica gel 60. The column was first eluted with CH_2Cl_2 to remove the starting products and then eluted with diethyl ether to furnish the bis(aza DTF) **12** as an amorphous material: 0.62 g, 0.87 mmol. − ^{1}H NMR (300 MHz): δ = 2.53, 2.60, 2.63, 2.70 (4 s, 12 H), 3.97 (m, 2 H), 6.99 (m, 4 H), 7.21 (m, 6 H), 7.34, 7.52, 7.64, 7.74, 8.16, 8.22 (6 d, J = 8.8 Hz, 6 H). − ^{13}C NMR: see Table 4. − MS: calcd. for $C_{35}H_{31}ClN_5O_2S_4$ m/z = 716.1049 [M + H$^+$]; found 716.1041.

The amine **2j** (0.7 g, 1.5 mmol) was added to a solution of 5-methyl-4-(methylthio)-2-piperidino-1,3-dithiolium iodide[8b] (0.7 g, 1.87 mmol) in anhydrous pyridine (10 mL). The mixture was refluxed for 1 h. After evaporation of the solvent, the crude product was treated with CH_2Cl_2, washed with H_2O and dried with Na_2SO_4. The residue was purified by column chromatography on silica gel with CH_2Cl_2 and then Et_2O as the eluents. This afforded compound **13** as an amorphous hemisolid (0.7 g, 75% yield). − ^{1}H NMR (200 MHz): δ = 2.16, 2.24 (2 s, 3 H), 2.25, 2.33 (2 s, 3 H), 2.57, 2.67 (2 s, 6 H), 3.93, 3.94 (2 s, 2 H), 6.97 (m, 4 H), 7.20 (m, 4 H), 7.61, 7.72, 8.12, 8.19 (4 d, J = 9 Hz, 4 H). − ^{13}C NMR (50.3 MHz): δ = 14.7, 15.5 (2 q, ^1J = 131 Hz), 19.3, 19.4 (2 q, ^1J = 141 Hz), 40.9 (tm, ^1J = 127 Hz), 44.6, 44.7 (2 qq, ^1J = 136 Hz, ^3J = 4.2 Hz), 113.4, 115.2 (2 t, ^3J = 4 Hz), 119.0 (m), 120.1, 120.2, 123.7, 123.8, 128.6, 128.8, 129.9 (non-quat. arom. C), 132.2, 132.7 (2 q, ^2J = 7.1 Hz), 137.5, 137.7 (2 m), 138.5, 139.1 (2 t, ^3J = 8.2 Hz), 144.3, 144.7 (2 m), 145.8, 146.1 (2 m), 148.6, 149.2, 149.3 (3 t, ^3J = 8.8 Hz), 159.6, 160.3, 164.0, 164.2 (4 s). − MS: calcd. for $C_{29}H_{27}N_4O_2S_5$ m/z = 623.0738 [M + H$^+$]; found 623.0738.

Trapping of Dimethyl Tetrathiooxalate 4: *tert*-Butyl isocyanide (0.66 g, 8 mmol) was added to a suspension of newly prepared $(NEt_4)_2C_2S_4$ (**3**; 1.65 g, 4 mmol) in dry $CHCl_3$ (50 mL). After cooling to −10 °C, the mixture was treated with MeI (1.14 g, 8 mmol) and maintained at 0 °C for 10 h. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography with petroleum ether and then diethyl ether as the eluents.

***N*-[4,5-Bis(methylthio)-1,3-dithiol-2-ylidene]*tert*-butylamine (5):** reddish oily product (0.58 g, 55% yield). − ^{1}H NMR (200 MHz): δ = 1.23 (s, 9 H), 2.35, 2.36 (2 s, 6 H). − ^{13}C NMR (50.3 MHz): δ = 17.9, 18.1 (2 q, ^1J = 141 Hz), 26.6 (qm, ^1J = 126 Hz), 57.1 (m), 122.7, 126.4 (2 q, ^3J = 5.2 Hz), 152.4 (s).

Hydrolysis of the Aza DTFs: A sample of **2a** or **2b** was maintained at room temperature under atmospheric moisture for several days. The dithiocarbamate **6** thus produced was suspended in MeOH and collected by filtration.

(Dimethylcarbamoyl)phenylmethyl *N-tert*-Butyldithiocarbamate (6a): M.p. 170 °C (CH_2Cl_2/Et_2O). − IR: $\tilde{\nu}$ = 3185 cm^{-1} (NH), 2990 (CH), 1622 (C=O), 1190 (C=S). − ^{1}H NMR (300 MHz): δ = 1.44 (s, 9 H), 3.00, 3.10 (2 s, 6 H), 5.94 (br, 1 H), 7.27−7.48 (m, 5 H), 8.00 (br, NH). − ^{13}C NMR (75.5 MHz): δ = 28.0 (qm, ^1J = 128 Hz), 36.5, 37.9 (2 qq, ^1J =139 Hz, ^3J = 3.2 Hz), 55.9 (dm, ^1J = 140 Hz), 57.4 (m), 128.1, 128.5, 128.9 (3 non-quat. arom. C), 135.3 (m), 170.1 (m), 192.3 (d, ^3J = 5.7 Hz). − MS: calcd. for $C_{15}H_{22}N_2OS_2$ m/z = 310.1173 [M$^{+\bullet}$]; found 310.1191; calcd. for $C_{10}H_{13}NOS$ m/z = 195.0718 [M − tBuNCS$^{+\bullet}$]; found 195.0714. − $C_{15}H_{22}N_2OS_2$ (310.47): calcd. C 58.03, H 7.14, N 9.02, S 20.65; found C 58.16, H 6.92, N 8.99, S 20.58.

(Dimethylcarbamoyl)phenylmethyl *N*-Isopropyldithiocarbamate (6b): M.p. 163 °C (MeOH). − IR: $\tilde{\nu}$ = 3173 cm^{-1} (NH), 2990 (CH), 1612 (C=O), 1155 (C=S). − ^{1}H NMR (200 MHz): δ = 1.18, 1.22

(2 d, $J = 6.2$ Hz, 6 H), 3.00, 3.12 (2 s, 6 H), 4.60 (m, 1 H), 6.16 (s, 1 H), 7.25−7.50 (m, 5 H), 8.24 (d, br, NH). − $C_{14}H_{20}N_2OS_2$ (296.45): calcd. C 56.72, H 6.80, N 9.45, S 21.63; found C 56.69, H 6.67, N 9.54, S 21.76.

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