[2+3] Cycloadditions of Azomethine Ylides with 1,3-Thiazole-5(4*H*)-thiones

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Dedicated to Professor *Max Viscontini* on the occasion of his 85th birthday

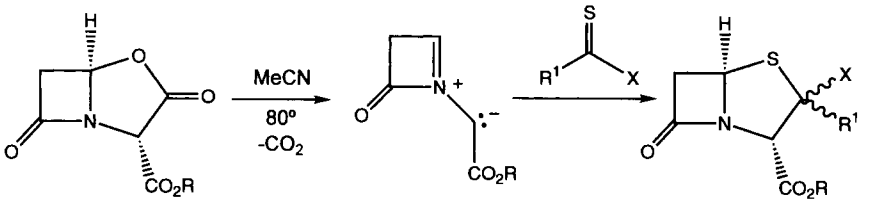
Thermal reactions of 1,2,3-trisubstituted aziridines **1** with 1,3-thiazole-5(4*H*)-thiones **6** in toluene yielded, in general, a mixture of two diastereoisomeric spirocyclic [2+3] cycloadducts. The formation of these products can be explained by a stereoselective electrocyclic ring opening of **1** to give an azomethine ylide **2** as the reactive intermediate, which is trapped immediately by **6** *via* a stereoselective 1,3-dipolar cycloaddition. Only in the case of *trans*-dimethyl 1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (*trans*-**1a**), four diastereoisomeric cycloadducts were formed (*Scheme 4*). This result is rationalized by an isomerization of the intermediate azomethine ylide *cis*-**2a** to *trans*-**2a**.

Introduction. – Azomethine ylides constitute a well-known class of 1,3-dipolar intermediates which were described for the first time by *Huisgen* and co-workers [1][2]. The classical experiments with thermal and photochemical ring opening of the stereoisomeric aziridines *cis*- and *trans*-**1a** confirm the preservation of orbital symmetry in these processes. With a series of additional experiments, the same authors demonstrated the use of thermally generated azomethine ylides of type **2** (*cf. Scheme 2*) for the preparation of five-membered heterocycles [3–6]. Simple procedures and the stereoselectivity of aziridine ring opening are attractive features of this concept. An increasing number of similar papers which showed further synthetic application emphasized the potential of this methodology in heterocyclic chemistry [7][8].

The generation of azomethine ylides is, however, not limited to the ring opening of aziridines. Other methods, *e.g.*, desilylation of α-silylonium salts [9], 1,2-prototropic rearrangement of α-amino-acid imines [10], and addition of carbenes or carbenoids onto imines [11] are now frequently used by numerous research groups. In the last few years, further reports have dealt with the use of thermally generated azomethine ylides from corresponding aziridines in syntheses of pyrrolidine and pyrrole derivatives [12]. Especially mentioned should be a recent publication which reports on a new method for the formation of carbapenams and carbapenems by utilizing an azomethine ylide as the reactive intermediate [13]. The same strategy has been used to synthesize penam and penem derivatives [14]. The intermediate azomethine ylide **4** was generated by thermal extrusion of CO_2 from the bicyclic 1,3-oxazolidinone **3** (*Scheme 1*). Trapping **4** by thiocarbonyl compounds furnished penam derivatives **5** in fair yields.

[1]) Visitor at the University of Zurich as a Swiss Federal scholar (*Bundesstipendiat*) from March to June 1995.

Scheme 1

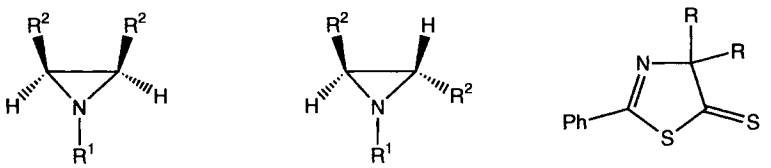


3 **4** **5**

Unlike olefinic and acetylenic dipolarophiles, thiocarbonyl compounds have been rarely explored in reactions with azomethine ylides (*cf.* [7][8][15]), but the results reported by *Gallagher* and co-workers [14] open new horizons in the synthetic use of [2+3] cycloadditions of azomethine ylides with thiocarbonyl compounds.

For many years, our research interest has been focused on different aspects of thiocarbonyl compounds, and their reactivity towards 1,3-dipoles is an essential part of current studies. Thus, reactions with diazo compounds [16], azides [17], thiocarbonyl ylides [18], carbonyl ylides [19], and thiocarbonyl *S*-imides [20] have been reported. Apart from aliphatic and aromatic thiones, 1,3-thiazole-5(4*H*)-thiones **6** belong to the most frequently used C=S derivatives in our studies. Very recently, we reported, in preliminary form, on the first example of a 1,3-dipolar cycloaddition of **6** with an azomethine ylide generated thermally from *cis*-1-methyl-2,3-diphenylaziridine (*cis*-**1b**) [21].

In this paper, we present complete results of the thermal reactions of aziridines **1a**, **1c**, and **1d** and 1,3-thiazole-5(4*H*)-thiones **6a** and **6b**.



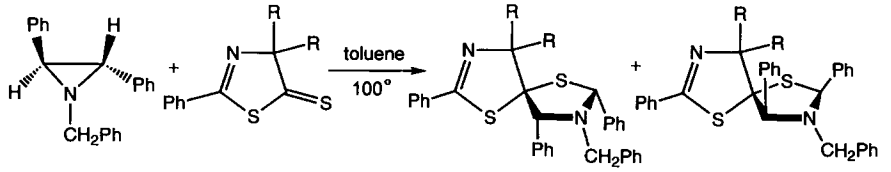
cis-**1a**	*trans*-**1a**	R^1 = 4-$MeOC_6H_4$, R^2 = CO_2Me	**6a** R = Me
cis-**1b**	-	R^1 = Me, R^2 = Ph	**b** R-R = -$(CH_2)_4$-
-	*trans*-**1c**	R^1 = $PhCH_2$, R^2 = Ph	
cis-**1d**	-	R^1 = 4-$MeOC_6H_4$, R^2 = Ph	

Results and Discussion. – All reactions of aziridines **1** with 1,3-thiazole-5(4*H*)-thiones **6** were carried out in toluene. After complete consumption of **6** (TLC), the solvent was removed and the crude reaction mixture was analyzed by ^{1}H-NMR spectroscopy. As characteristic signals, located at 6–4 ppm, the absorptions of the H-atoms of the newly formed thiazolidine ring were used to determine the yield and ratio of the isomeric cycloadducts.

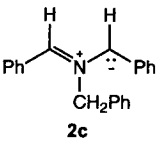
As an extension of previous results obtained with *cis*-**1b** [21], we used the *trans*-configured aziridine *trans*-**1c** in reactions with **6a** and **6b**. In both cases, mixtures of two

isomeric products with similar ratio (3:1 and 4:1, resp.) were detected. After chromatographic separation, the crystalline cycloadducts **7** and **8** were obtained (*Scheme 2*). The structures of the pair of diastereoisomers **7a**/**8a** were elucidated by X-ray crystallography (*Fig. 1*). As expected, in both isomers, the Ph groups of the 1,3-thiazolidine ring are *cis*-configured. This result can be rationalized on the basis of a stereoselective ring opening of *trans*-**1c** yielding the intermediate azomethine ylide **2c**. A fast interception by **6a** prevents the ylide from isomerization, and, therefore, no 'false isomers' of cycloadducts were formed. The major product **7a** is the sterically less hindered one with the Ph groups located opposite to the geminal Me groups.

Scheme 2



trans-**1c** **6a** R = Me, **b** R-R = -(CH$_2$)$_4$- **7a** R = Me, **b** R-R = -(CH$_2$)$_4$- **8a** R = Me, **b** R-R = -(CH$_2$)$_4$-



2c

We propose that the major product of the reaction of *trans*-**1c** and **6b** is again the sterically less hindered **7b**. Isomers **7b** and **8b** show characteristic differences in the chemical shifts ($\Delta\delta$) of the H-atoms of the 1,3-thiazolidine ring: whereas $\Delta\delta$ in **7b** is 0.62 ppm, its value in **8b** is 0.79 ppm. Similar differences were observed for **7a** ($\Delta\delta$ = 0.53 ppm) and **8a** ($\Delta\delta$ = 0.90 ppm)[2]). There is also a remarkable difference in the shifts of the cyclopentane CH_2 groups: the shielding effect of the Ph groups in **8b** gives rise to an upfield shift of signals attributed to CH_2 groups of the cyclopentane ring.

Unexpectedly, the reaction of triarylaziridine *cis*-**1d** with **6a** yielded only a single cycloadduct for which we propose structure **9a** (*Scheme 3*). Reliable criteria for the assignment of the configuration are the chemical shifts of the geminal Me groups of the dihydro-1,3-thiazole ring (*Fig. 2*): in both isomers with the Ph group at C(9) in a *cis*-position with respect to the geminal Me groups at C(4), *i.e.*, in **8a** (*Scheme 2*) and **10c** [21], the absorptions of $Me_2C(4)$ are shifted towards high field. The chemical shifts observed in **9a** correspond very well with those of **9c** [21] and exclude the isomeric structure **10a**.

In the case of the reaction of *cis*-**1d** with **6b**, the analysis of the crude mixture showed the presence of a predominant product **9b** accompanied by traces of a second isomer,

[2]) In both cases, the isomer of type **8** shows the larger R_f value (TLC, SiO_2).

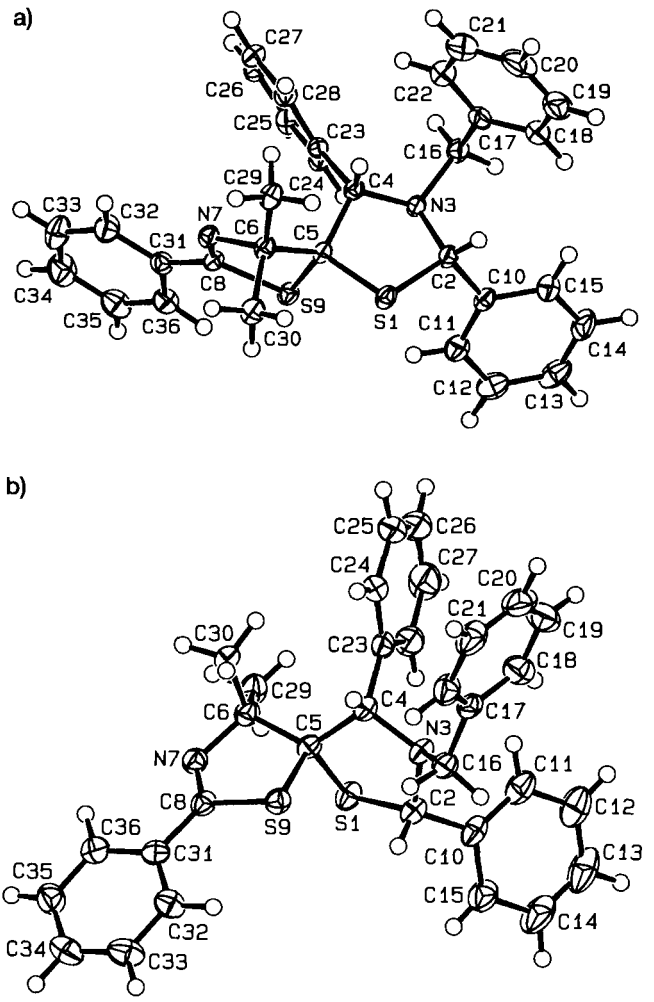


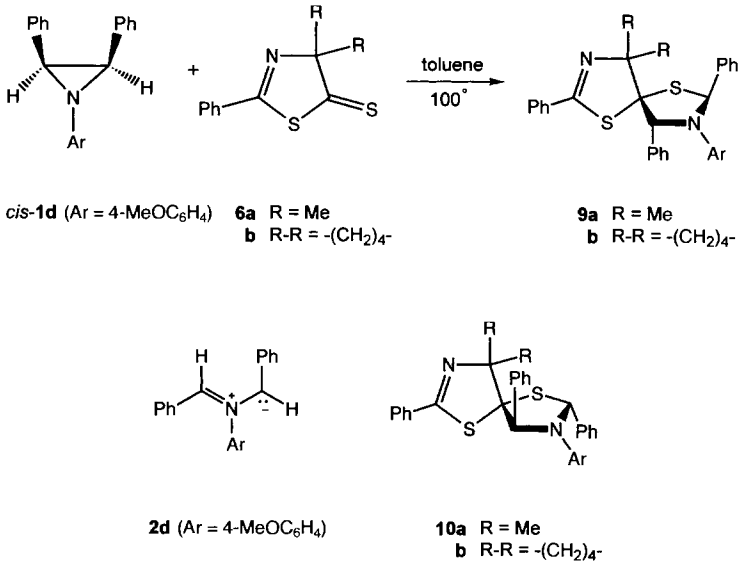
Fig. 1. *ORTEP Plots* [22] *of the molecular structures of* a) *one of the two independent molecules of* **7a** *and* b) **8a** (with 50% probability ellipsoids)

most likely **10b**. The arguments for the assignment of the structure **9b** are analogous to the case of the isomers of type **9** and **10** discussed above.

Finally, we performed reactions of the *cis*- and *trans*-aziridinedicarboxylates, *cis*-**1a** and *trans*-**1a**, respectively, with **6a** and **6b**. Thermal ring opening of *cis*-**1a** results in the formation of *trans*-**2a**, as shown by *Huisgen* in his pioneering work [1–3] (*Scheme 4*). Interception with **6a** or **6b** afforded mixtures of two isomeric cycloadducts in ratios of *ca.* 4:1. In accordance with results presented in *Schemes 2* and *3*, we propose the sterically less hindered structures **9d** and **9e** for the major products and **10d** and **10e** for the minor ones.

The analogous reaction of **6a** with *trans*-**1a** yielded not only the expected cycloadducts **7d** and **8d**, but also *ca.* 16% of a 3:1 mixture of **9d** and **10d** (*Scheme 4*). This was the only

Scheme 3



experiment in which 'false stereoisomers' of 1:1 cycloadducts with 1,3-thiazole-5(4*H*)-thiones were obtained. The isomers **7d** and **8d** were found in the crude reaction mixture as major products in a ratio of *ca.* 2:1. By chromatographic workup, the fraction with **7d** and **8d** was separated from the minor components **9d** and **10d**. However, complete

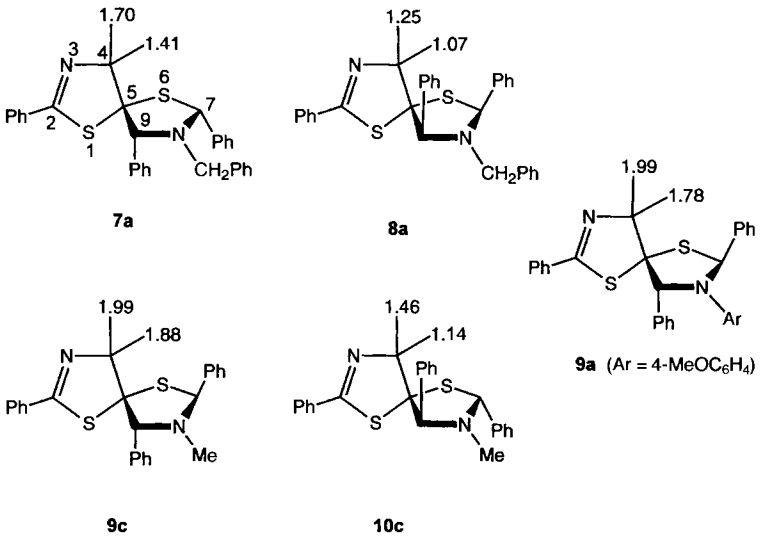
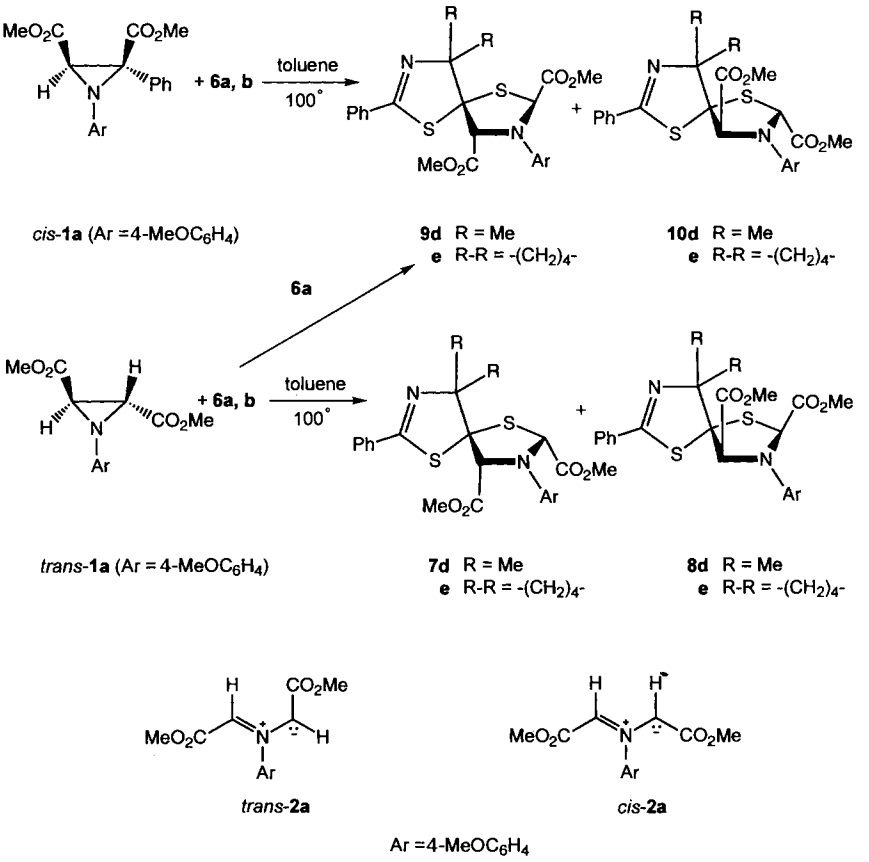


Fig. 2. *^{1}H-NMR Chemical shifts of 2 Me–C(4) in some spirocyclic 4,5-dihydro-1,3-thiazole derivatives* (300 MHz, $CDCl_3$)

Scheme 4



separation of **7d** and **8d** could not be achieved using prep. TLC. Therefore, their mixture was used for spectroscopic characterization.

In the case of the reaction of *trans*-**1a** with **6b**, we observed formation of only two cycloadducts, in contrast to the experiment with **6a**. The diastereoisomers **7e** and **8e** were formed in a ratio of *ca.* 3:1. This mixture was separated using prep. TLC, yielding pure products.

In conclusion, the experiments described above show once more that 1,3-thiazole-5(4*H*)-thiones **6** can be used for efficient trapping of 1,3-dipoles generated as reactive intermediates. Azomethine ylides **2** afforded cycloadducts in good yields, and in almost all cases, mixtures of only two diastereoisomers were formed. Thus, thermal ring opening of aziridines **1** occurs stereoselectively following orbital symmetry rules [23][24]. Azomethine ylides formed in these processes are trapped immediately by **6** without isomerization. The only exception was found in the reaction of *trans*-**1a** with **6a**. This observation is in accordance with the previously described behavior of *trans*-**1a** in reactions with symmetrical C,C-dipolarophiles [3]. Unlike the isomeric *cis*-**1a**, *trans*-**1a** afforded mix-

tures of 'expected' and 'false' cycloadducts when less reactive dipolarophiles were used [3]). The reason for the formation of 'false' cycloadducts **9d** and **10d** is an isomerization of the azomethine ylide *cis*-**2a** into *trans*-**2a** before interception by **6a** [4]).

We thank the analytical sections of the Institute of Organic Chemistry of the University of Zürich for spectra and analyses. Financial support by the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged. *G.M.* thanks the *Swiss Federal Commission for Foreign Students* for a scholarship.

Experimental Part

General. See [25]. M.p.: in capillary; *Büchi-SMP-125* apparatus; uncorrected. IR (KBr, unless otherwise stated): *Perkin-Elmer 781*. NMR ($CDCl_3$): *Bruker AC 300* (^1H, 300 MHz) and *Bruker ARX 300* (^{13}C, 75.5 MHz). CI-MS (NH_3): *Varian MAT-112S*. Elemental analyses were performed by the Mikroanalytisches Laboratorium des Organisch-chemischen Instituts der Universität Zürich.

1. *Starting Materials.* Aziridines **1** were prepared according to known procedures: *cis*- and *trans*-dimethyl 1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (*cis*- and *trans*-**1a**, resp.) [1], *trans*-1-benzyl-2,3-diphenylaziridine (*trans*-**1c**) [6], and *cis*-1-(4-methoxyphenyl)-2,3-diphenylaziridine (*cis*-**1d**) [26]. 1,3-Thiazole-5(4*H*)-thiones **6a** and **6b** were prepared according to [27] and [28], resp.

2. *Reactions of Aziridines* **1** *with 1,3-Thiazole-5(4H)-thiones* **6**. 2.1. *General Procedure.* A stirred soln. of aziridine **1** (1.1 mmol) and 1,3-thiazole-5(4*H*)-thione **6** (1 mmol) in abs. toluene (1 ml) was heated to 100° (oil bath). After *ca.* 20 h, the solvent was evaporated, the residue dissolved in $CDCl_3$, and a weighed amount of 1,1,2,2-tetrachloroethane was added as a standard to establish the yields of the products in the crude mixture by ^1H-NMR spectroscopy (*s* for 2 H at 5.92 ppm). Then, the soln. was concentrated, and the products were separated by prep. TLC (SiO_2). Anal. pure samples of the products were obtained by recrystallization from alcoholic solvents.

2.2. *Reaction of* trans-**1c** *with* **6a**. ^1H-NMR: **7a**/**8a** 75:25. *(5RS,7RS,9RS)-8-Benzyl-4,4-dimethyl-2,7,9-triphenyl-1,6-dithia-3,8-diazaspiro[4.4]non-2-ene* (**7a**). Isolated as the more polar fraction (hexane/Et_2O 4:1, twofold development) as a colorless oil which solidified at r.t. (3 d): 360 mg (71%). Recrystallization from MeOH/CH_2Cl_2 yielded colorless crystals. M.p. 116–118°. IR: 3040*m*, 2980*w*, 2860*w*, 1595*s*, 1575*m* (C=N), 1490*s*, 1450*s* (br.), 1260*s*, 1175*m*, 1075*m*, 1065*m*, 1030*m*, 950*vs*, 910*m*, 750*s*, 700*vs*, 690*vs*, 665*s*. ^1H-NMR: 7.8–6.85 (*m*, 20 arom. H); 5.03, 4.50 (2*s*, H–C(7), H–C(9)); 3.66, 3.57 (*AB*, J = 14.6, CH_2); 1.70, 1.41 (2*s*, Me_2C). ^{13}C-NMR: 166.9 (C=N); 140.1, 137.3, 133.9, 133.2 (4*s*, 4 arom. C); 131.1, 130.7, 130.3, 128.7, 128.4, 128.2, 128.0, 127.9, 127.6, 127.3 (10*d*, 20 arom. CH); 86.3, 79.5 (2*s*, C(4), C(5)); 72.8, 66.9 (2*d*, C(7), C(9)); 51.3 (*t*, CH_2); 25.8, 22.2 (2*q*, Me_2C). CI-MS: 508 (40), 507 (100, $[M+1]^+$), 391 (6). Anal. calc. for $C_{32}H_{30}N_2S_2$ (506.73): C 75.85, H 5.97, N 5.53, S 12.65; found: C 75.96, H 5.94, N 5.46, S 12.37.

Suitable crystals for an X-ray crystal-structure determination were grown from EtOH.

(5RS,7SR,9SR)-8-Benzyl-4,4-dimethyl-2,7,9-triphenyl-1,6-dithia-3,8-diazaspiro[4.4]non-2-ene (**8a**). Isolated as the less polar fraction (hexane/Et_2O 4:1, twofold development) as a colorless oil which solidified at −20° overnight: 95 mg (19%). Recrystallization from EtOH yielded colorless crystals. M.p. 130–131°. IR: 3020*w*, 2800*w*, 1600*m* (C=N), 1490*m*, 1450*m*, 1260*s*, 1170*m*, 1120*m* (br.), 950*s*, 775*m*, 750*s*, 690*vs* (br.), 610*m*. ^1H-NMR: 7.8–7.1 (*m*, 20 arom. H); 5.53, 4.63 (2*s*, H–C(7), H–C(9)); 3.87, 3.76 (*AB*, J = 13.7, CH_2); 1.25, 1.07 (2*s*, Me_2C). ^{13}C-NMR: 164.0 (*s*, C=N); 142.0, 137.8, 137.0, 133.6 (4*s*, 4 arom. C); 131.1, 130.7, 129.3, 128.6, 128.5, 128.4, 128.1, 128.0, 127.6, 127.2, 127.1 (11*d*, 20 arom. CH); 92.7, 78.7 (2*s*, C(4), C(5)); 73.8, 73.0 (2*d*, C(7), C(9)); 55.4 (*t*, CH_2); 25.8, 20.3 (2*q*, Me_2C). CI-MS: 508 (39), 507 (100, $[M+1]^+$). Anal. calc. for $C_{32}H_{30}N_2S_2$ (506.73): C 75.85, H 5.97, N 5.53, S 12.65; found: C 76.11, H 6.32, N 5.42, S 12.40.

Suitable crystals for an X-ray crystal-structure determination were grown from EtOH.

2.3. *Reaction of* trans-**1c** *with* **6b**. ^1H-NMR: **7b**/**8b** 80:20. *(2RS,4RS,5RS)-3-Benzyl-2,4,12-triphenyl-1,13-dithia-3,11-diazadispiro[4.0.4.3]tridec-11-ene* (**7b**). Isolated as the more polar fraction (hexane/Et_2O 9:1, twofold development) as a viscous, colorless oil: 320 mg (60%). Recrystallization from MeOH yielded colorless crystals. M.p. 170–171°. IR: 2970*s*, 1595*s*, 1575*s* (C=N), 1490*s*, 1450*s* (br.), 1310*m*, 1255*s* (br.), 1200*m*, 1120*s* (br.), 1065*s*

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[3]) Only ethenetetracarbonitrile and dimethyl acetylenedicarboxylate (dimethyl but-2-ynedioate) exclusively gave 'expected' interception products [3].

[4]) The chromatographically isolated mixture **7d**/**8d** remained unchanged after heating in toluene to 100° for 3 h.

(br.), 1025*s*, 960*vs*, 920*s*, 750*vs*, 695*vs*, 660*m*. ^{1}H-NMR: 7.8–6.85 (*m*, 20 arom. H); 5.06, 4.44 (2*s*, H–C(7), H–C(9)); 3.72, 3.58 (*AB*, J = 14.0, PhCH_2); 2.55–2.4, 2.25–1.55 (2*m*, 1:7, 4 CH_2). ^{13}C-NMR: 166.7 (*s*, C=N); 140.6, 136.2, 133.7, 133.3 (4*s*, 4 arom. C); 131.4, 130.5, 130.3, 128.7, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.3, 127.1 (12*d*, 20 arom. CH); 89.8, 84.8 (2*s*, C(5), C(6)); 74.7, 66.5 (2*d*, C(2), C(4)); 51.1 (*t*, PhCH_2); 41.2, 31.8, 25.4, 23.9 (4*t*, 4 CH_2). CI-MS: 534 (40), 533 (100, $[M + 1]^+$), 441 (7). Anal. calc. for $C_{34}H_{32}N_2S_2$ (532.77): C 76.65, H 6.06, N 5.26, S 12.04; found: C 76.95, H 6.38, N 5.50, S 12.42.

*(2*RS,*4*RS,*5*SR*)-3-Benzyl-2,4,12-triphenyl-1,13-dithia-3,11-diazadispiro[4.0.4.3]tridec-11-ene* (**8b**). Isolated as the slightly less polar fraction (hexane/Et_2O 9:1, twofold development) as a viscous, colorless oil: 110 mg (21%). IR (neat): 2980*s*, 1590*s* (C=N), 1480*s*, 1430*s* (br.), 1250*s* (br.), 1205*s*, 1140*s* (br.), 1020*s* (br.), 1000*s*, 940*vs*, 760*s*, 630*s*. ^{1}H-NMR: 7.75–6.9 (*m*, 20 arom. H); 5.38, 4.59 (2*s*, H–C(7), H–C(9)); 3.93, 3.78 (*AB*, J = 14.9, PhCH_2); 2.65–2.5, 2.1–1.0 (2*m*, 1:7, 4 CH_2). ^{13}C-NMR: 163.6 (*s*, C=N); 139.0, 138.1, 135.2, 133.9 (4*s*, 4 arom. C); 130.8, 130.5, 129.8, 128.7, 128.5, 128.2, 127.9, 127.8, 127.7, 127.4, 127.2 (11*d*, 20 arom. CH); 90.2, 89.4 (2*s*, C(5), C(6)); 77.0, 70.9 (2*d*, C(2), C(4)); 53.7 (*t*, PhCH_2); 38.9, 33.4, 25.3, 25.0 (4*t*, 4 CH_2). CI-MS: 534 (35), 533 (100, $[M + 1]^+$). Anal. calc. for $C_{34}H_{32}N_2S_2$ (532.77): C 76.65, H 6.06, N 5.26, S 12.04; found: C 76.93, H 5.78, N 5.45, S 11.79.

2.4. *Reaction of* cis-**1d** *with* **6a**. ^{1}H-NMR: Only **9a** was detected. Chromatography (hexane/Et_2O 4:1) yielded 410 mg (79%) of *(5*RS,*7*SR,*9*RS*)-8-(4-methoxyphenyl)-4,4-dimethyl-2,7,9-triphenyl-1,6-dithia-3,8-diazaspiro[4.4]non-2-ene* (**9a**) as a viscous, colorless oil. Crystallization from EtOH gave colorless crystals. M.p. 84–86°. IR: 2980*w*, 2930*w*, 1595*m* (C=N), 1510*vs*, 1450*m*, 1245*vs*, 1170*m*, 1035*m*, 955*s*, 825*m*, 765*m*, 695*s*. ^{1}H-NMR: 7.6–7.55 (*m*, 5 arom. H); 7.4–7.15 (*m*, 10 arom. H); 6.57, 6.49 (*AA'BB'*, J = 8.9, 4 arom. H); 6.14, 5.66 (2*s*, H–C(7), H–C(9)); 3.57 (*s*, MeO); 1.99, 1.78 (2*s*, Me_2C). ^{13}C-NMR: 164.7 (*s*, C=N); 154.4, 138.7, 138.3, 137.9, 133.3 (5*s*, 5 arom. C); 131.0, 128.9, 128.4, 128.2, 127.9, 127.8, 127.5, 123.2, 113.7 (9*d*, 19 arom. CH); 85.2, 82.0 (2*s*, C(5), C(6)); 75.9, 68.0 (2*d*, C(7), C(9)); 55.1 (*q*, MeO); 26.4, 23.1 (2*q*, Me_2C). CI-MS: 524 (36), 523 (100, $[M + 1]^+$), 280 (16), 244 (12). Anal. calc. for $C_{32}H_{30}N_2OS_2$ (522.73): C 73.53, H 5.78, N 5.36, S 12.27; found: C 73.18, H 5.61, N 5.28, S 11.95.

2.5. *Reaction of* cis-**1d** *with* **6b**. ^{1}H-NMR: **9b**/**10b** 97:3. After chromatographic workup (hexane/Et_2O 17:3), only the major product could be isolated as a viscous, colorless oil: 370 mg (68%) of *(2*RS,*4*SR,*5*SR*)-3-(4-methoxyphenyl)-2,4,12-triphenyl-1,13-dithia-3,11-diazadispiro[4.0.4.3]tridec-11-ene* (**9b**). Crystallization from MeOH at −20° yielded colorless crystals. M.p. 136–138°. IR: 2950*m*, 1590*m*, 1570*m* (C=N), 1510*m*, 1455*s*, 1240*vs*, 1180*m*, 1040*s*, 945*m*, 920*m*, 825*m*, 760*s*, 695*vs*. ^{1}H-NMR: 7.6–7.15 (*m*, 15 arom. H); 6.59, 6.51 (*AA'BB'*, J = 9.0, 4 arom. H); 6.24, 5.70 (2*s*, H–C(7), H–C(9)); 3.60 (*s*, MeO); 3.05–2.9, 2.7–2.5, 2.3–1.8 (3*m*, 1:2:5, 4 CH_2). ^{13}C-NMR: 165.1 (C=N); 154.1, 139.1, 138.1, 138.0, 133.4 (5*s*, 5 arom. C); 130.9, 129.3, 128.4, 128.2, 127.9, 127.8, 127.7, 127.6, 123.1, 113.5 (10*d*, 19 arom. CH); 92.9, 83.5 (2*s*, C(5), C(6)); 76.6, 68.2 (2*d*, C(2), C(4)); 55.0 (*q*, MeO); 39.0, 32.5, 25.5, 24.3 (4*t*, 4 CH_2). CI-MS: 550 (35), 549 (100, $[M + 1]^+$), 302 (11), 248 (11), 244 (17), 212 (16). Anal. calc. for $C_{34}H_{32}N_2OS_2$ (548.77): C 74.41, H 5.88, N 5.11, S 11.68; found: C 74.69, H 5.95, N 5.03, S 11.47.

2.6. *Reaction of* cis-**1a** *with* **6a**. ^{1}H-NMR: **9d**/**10d** 80:20. *Dimethyl (5*RS,*7*SR,*9*RS*)-8-(4-Methoxyphenyl)-4,4-dimethyl-2-phenyl-1,6-dithia-3,8-diazaspiro[4.4]non-2-ene-7,9-dicarboxylate* (**9d**). Isolated as the less polar fraction (hexane/Et_2O 4:1, twofold development) as a viscous, colorless oil: 230 mg (47%). Crystallization from EtOH gave colorless crystals. M.p. 161–162°. IR: 2950*w*, 1760*m*, 1735*vs* (br., C=O), 1590*w*, 1575*w* (C=N), 1515*vs* (br.), 1445*m*, 1435*m*, 1250*vs* (br.), 1200*s*, 1170*vs*, 1040*s*, 1010*s*, 955*s*, 820*s*, 770*s*. ^{1}H-NMR: 7.75–7.7 (*m*, 2 arom. H); 7.5–7.35 (*m*, 3 arom. H); 6.8–6.7 (*m*, 4 arom. H); 5.63, 5.34 (2*s*, H–C(7), H–C(9)); 3.75, 3.72, 3.61 (3*s*, 3 MeO); 1.88, 1.54 (2*s*, Me_2C). ^{13}C-NMR: 170.2, 169.9 (2*s*, 2 C=O); 164.0 (*s*, C=N); 154.6, 137.5, 132.9 (3*s*, 3 arom. C); 131.5, 128.5, 127.9, 118.5, 114.8 (5*d*, 9 arom. CH); 82.0, 79.9 (2*s*, C(4), C(5)); 72.6, 63.3 (2*d*, C(7), C(9)); 55.4, 52.7, 51.7 (3*q*, 3 MeO); 24.7, 21.7 (2*q*, Me_2C). CI-MS: 488 (31), 487 (100, $[M + 1]^+$). Anal. calc. for $C_{24}H_{26}N_2O_5S_2$ (486.61): C 59.24, H 5.39, N 5.76, S 13.18; found: C 58.91, H 5.50, N 5.45, S 13.07.

*Dimethyl (5*RS,*7*RS,*9*SR*)-8-(4-Methoxyphenyl)-4,4-dimethyl-2-phenyl-1,6-dithia-3,8-diazaspiro[4.4]non-2-ene-7,9-dicarboxylate* (**10d**). Isolated as the slightly more polar fraction (hexane/Et_2O 4:1, twofold development) as a viscous, colorless oil: 63 mg (13%). Crystallization from EtOH gave colorless crystals. M.p. 157–159°. IR: 2950*m*, 1770*vs* (C=O), 1735*vs* (C=O), 1595*m*, 1575*m* (C=N), 1515*vs* (br.), 1450*m*, 1435*m*, 1330*m*, 1260*vs* (br.), 1160*vs* (br.), 1040*s*, 955*s*, 815*s*, 765*s*, 680*s*. ^{1}H-NMR: 7.8–7.75 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 6.83, 6.69 (*AA'BB'*, J = 9.0, 4 arom. H); 5.53, 5.21 (2*s*, H–C(7), H–C(9)); 3.80, 3.75, 3.65 (3*s*, 3 MeO); 1.61, 1.56 (2*s*, Me_2C). ^{13}C-NMR: 170.4, 169.4 (2*s*, 2 C=O); 164.1 (*s*, C=N); 154.2, 137.7, 133.2 (3*s*, 3 arom. C); 131.3, 128.4, 128.0, 117.3, 114.8 (5*d*, 9 arom. CH); 87.6, 77.2 (2*s*, C(4), C(5)); 72.7, 63.0 (2*d*, C(2), C(9)); 55.4, 52.8, 52.2 (3*q*, 3 MeO); 25.2, 21.2 (2*q*, Me_2C). CI-MS: 488 (27), 487 (100, $[M + 1]^+$), 262 (11), 226 (8). Anal. calc. for $C_{24}H_{26}N_2O_5S_2$ (486.61): C 59.24, H 5.39, N 5.76, S 13.18; found: C 59.14, H 5.43, N 5.72, S 13.23.

2.7. *Reaction of* cis-**1a** *with* **6b**. ^{1}H-NMR: **9e**/**10e** 85:15. *Dimethyl (2*RS,*4*SR,*5*SR*)-3-(4-Methoxyphenyl)-12-phenyl-1,13-dithia-3,11-diazadispiro[4.0.4.3]tridec-11-ene-2,4-dicarboxylate* (**9e**). Isolated as the less polar fraction (hexane/Et_2O 17:3) as a viscous, colorless oil which solidified at r.t.: 380 mg (74%). Crystallization from EtOH with small amounts of CH_2Cl_2 gave colorless crystals. M.p. 118–120°. IR: 2950*m*, 1755v*s* (br., C=O), 1595*w*, 1575*m* (C=N), 1510v*s*, 1450*s*, 1435*s*, 1335*s*, 1270v*s*, 1250v*s*, 1195v*s*, 1170v*s*, 1035*m*, 985*m*, 950*m*, 900*m*, 815*s*, 770*s*, 690*m*. ^{1}H-NMR: 7.65–7.6 (*m*, 2 arom. H); 7.35–7.25 (*m*, 3 arom. H); 6.66, 6.57 (*AA'BB'*, *J* = 9.4, 4 arom. H); 5.67, 5.29 (2*s*, H–C(2), H–C(4)); 3.74, 3.71, 3.57 (3*s*, 3 MeO); 2.8–1.7 (*m*, 4 CH_2). ^{13}C-NMR: 170.1, 169.8 (2*s*, 2 C=O); 165.0 (*s*, C=N); 154.6, 137.5, 133.2 (3*s*, 3 arom. C); 131.4, 128.5, 128.0, 118.6, 114.7 (5*d*, 9 arom. CH); 93.0, 78.9 (2*s*, C(5), C(6)); 74.0, 63.4 (2*d*, C(2), C(4)); 55.4, 52.8, 51.6 (3*q*, 3 MeO); 38.1, 30.9, 25.2, 24.4 (4*t*, 4 CH_2). CI-MS: 514 (28), 513 (100, $[M + 1]^+$), 288 (7), 248 (9). Anal. calc. for $C_{26}H_{28}N_2O_5S_2$ (512.65): C 60.91, H 5.51, N 5.47, S 12.51; found: C 60.59, H 5.87, N 5.28, S 12.33.

*Dimethyl (2*RS,*4*SR,*5*RS*)-3-(4-Methoxyphenyl)-12-phenyl-1,13-dithia-3,11-diazadispiro[4.0.4.3]tridec-11-ene-2,4-dicarboxylate* (**10e**). Isolated as the slightly less polar fraction (hexane/Et_2O 17:3) as a viscous, colorless oil, contaminated with *ca.* 20% of **9e**[5]). ^{1}H-NMR: 7.85–7.8 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 6.81, 6.68 (*AA'BB'*, *J* = 9.1, 4 arom. H); 5.52, 5.22 (2*s*, H–C(2), H–C(4)); 3.80, 3.73, 3.61 (3*s*, 3 MeO); 2.3–1.7 (*m*, 4 CH_2). ^{13}C-NMR: 170.7, 169.5 (2*s*, 2 C=O); 165.0 (*s*, C=N); 154.2, 137.7, 133.3 (3*s*, 3 arom. C); 131.4, 128.4, 128.0, 117.3, 114.9 (5*d*, 9 arom. CH); 87.7, 85.3 (2*s*, C(5), C(6)); 73.8, 63.1 (2*d*, C(2), C(4)); 55.4, 52.9, 52.2 (3*q*, 3 MeO); 37.6, 34.0, 25.0, 24.5 (4*t*, 4 CH_2).

2.8. *Reaction of* trans-**1a** *with* **6b**. ^{1}H-NMR: **7e**/**8e** 75:25. *Dimethyl (2*RS,*4*RS,*5*RS*)-3-(4-Methoxyphenyl)-12-phenyl-1,13-dithia-3,11-diazadispiro[4.0.4.3]tridec-11-ene-2,4-dicarboxylate* (**7e**). Isolated as the more polar fraction (hexane/Et_2O 4:1) as a viscous, colorless oil: 280 mg (55%). IR (neat): 2950*m*, 1740v*s* (br., C=O), 1595*w*, 1575*w* (C=N), 1510v*s*, 1445*m*, 1430*m*, 1250v*s* (br.), 1195*s*, 1165*s*, 1035*m*, 810*m*, 765*m*. ^{1}H-NMR: 7.8–7.7 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 6.85, 6.67 (*AA'BB'*, *J* = 9.1, 4 arom. H); 5.44, 5.04 (2*s*, H–C(2), H–C(4)); 3.79, 3.73, 3.60 (3*s*, 3 MeO); 2.35–1.65 (*m*, 4 CH_2). ^{13}C-NMR: 169.7, 169.5 (2*s*, 2 C=O); 164.9 (*s*, C=N); 153.8, 138.4, 133.2 (3*s*, 3 arom. C); 131.5, 128.5, 128.1, 115.6, 114.9 (5*d*, 9 arom. CH); 92.7, 80.3 (2*s*, C(5), C(6)); 72.6, 64.7 (2*d*, C(2), C(4)); 55.5, 52.9, 52.1 (3*s*, 3 MeO); 38.4, 32.7, 25.0, 24.1 (4*t*, 4 CH_2). CI-MS: 514 (31), 513 (100, $[M + 1]^+$), 391 (7), 288 (19), 226 (10). Anal. calc. for $C_{26}H_{28}N_2O_5S_2$ (512.65): C 60.91, H 5.51, N 5.47, S 12.51; found: C 60.94, H 5.65, N 5.21, S 12.43.

*Dimethyl (2*RS,*4*RS,*5*SR*)-3-(4-Methoxyphenyl)-12-phenyl-1,13-dithia-3,11-diazadispiro[4.0.4.3]tridec-11-ene-2,4-dicarboxylate* (**8e**). Isolated as the slightly less polar fraction (hexane/Et_2O 4:1) as a viscous, colorless oil: 85 mg (17%). IR ($CHCl_3$): 2960*m*, 1750v*s* (C=O), 1730v*s* (C=O), 1595*w*, 1575*w* (C=N), 1510v*s*, 1435*m*, 1250v*s*, 1170*s*, 1040*m*, 975*m*. ^{1}H-NMR: 7.75–7.7 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 6.77, 6.75 (*AA'BB'*, *J* = 9.3, 4 arom. H); 5.67, 5.11 (2*s*, H–C(2), H–C(4)); 3.76, 3.75 (2*s*, 1:2, 3 MeO); 2.35–1.75 (*m*, 4 CH_2). ^{13}C-NMR: 169.2, 169.0 (2*s*, 2 C=O); 162.7 (*s*, C=N); 153.7, 138.5, 133.3 (3*s*, 3 arom. C); 131.4, 128.1, 126.1, 115.4, 115.0 (5*d*, 9 arom. CH); 88.4, 87.9 (2*s*, C(5), C(6)); 71.5, 64.1 (2*d*, C(2), C(4)); 55.1, 52.9, 52.5 (3*s*, 3 MeO); 36.7, 35.4, 25.1, 25.0 (4*t*, 4 CH_2). CI-MS: 514 (31), 513 (100, $[M + 1]^+$), 391 (9), 376 (9), 288 (21), 248 (7), 226 (12), 138 (6). Anal. calc. for $C_{26}H_{28}N_2O_5S_2$ (512.65): C 60.91, H 5.51, N 5.47, S 12.51; found: C 60.53, H 5.75, N 5.00, S 12.48.

2.9. *Reaction of* trans-**1a** *with* **6a**. A stirred soln. of *trans*-**1a** (291 mg, 1.1 mmol) and **6a** (221 mg, 1 mmol) in toluene (1 ml) was heated to 80° for 11 h. After that time, no *trans*-**1a** was present in the mixture (TLC). After evaporation, the ^{1}H-NMR revealed the presence of **7a**/**8d**/**9d**/**10d** 58:26:12:4 in a total yield of 67% (1,1,2,2-tetrachloroethane as standard). Prep. TLC (SiO_2, hexane/Et_2O 3:2) afforded 260 mg (54%) of **7d**/**8d** 2:1 which could not be separated[6]). The minor components **9d** and **10d** were isolated as pure compounds (34 mg (7%) and 10 mg (2%), resp.).

7d: ^{1}H-NMR: 7.80–7.77 (*m*, 2 arom. H); 7.47–7.37 (*m*, 3 arom. H); 6.84, 6.80 (*AA'BB'*, *J* = 9.1, 4 arom. H); 5.41, 5.14 (2*s*, H–C(2), H–C(4)); 3.78, 3.75, 3.67 (3*s*, 3 MeO); 1.56, 1.49 (2*s*, Me_2C). ^{13}C-NMR: 169.6, 169.5 (2*s*, 2 C=O); 165.6 (*s*, C=N); 153.7, 138.2, 132.8 (3*s*, 3 arom. C); 131.8, 128.6, 128.3, 115.3, 115.0 (5*d*, 9 arom. CH); 81.8, 81.1 (2*s*, C(5), C(6)); 70.4, 64.0 (2*d*, C(2), C(4)); 55.6, 52.9, 52.3 (3*q*, 3 MeO); 24.8, 22.7 (2*q*, Me_2C).

8d: ^{1}H-NMR: 7.74–7.71 (*m*, 2 arom. H); 7.47–7.37 (*m*, 3 arom. H); 6.88, 6.68 (*AA'BB'*, *J* = 9.1, 4 arom. H); 5.67, 5.08 (2*s*, H–C(2), H–C(4)); 3.80, 3.77, 3.76 (3*s*, 3 MeO); 1.51, 1.75 (2*s*, Me_2C). ^{13}C-NMR: 169.2, 168.8 (2*s*, 2 C=O); 163.0 (*s*, C=N); 153.5, 138.2, 132.7 (3*s*, 3 arom. C); 131.6, 128.6, 128.3, 115.0, 114.9

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[5]) Even after repeated chromatography (prep. TLC), **10e** could not be obtained in pure form. Therefore, the NMR data stem from a sample of **10e** containing *ca.* 20% of **9e**.

[6]) The NMR data of **7d** and **8d** are taken from a spectrum of the 2:1 mixture.

(5*d*, 9 arom. CH); 104.1, 90.6 (2*s*, C(5), C(6)); 70.7, 63.8 (2*d*, C(2), C(4)); 55.6, 52.9, 52.4 (3*q*, 3 MeO); 26.0, 21.7 (2*q*, Me_2C).

Data of **7d**/**8d** 2:1: IR (neat): 3000*m*, 2950*m*, 1750*vs* (br.), 1515*vs*, 1445*s*, 1260*vs*, 1175*vs*, 1040*s*, 955*s*, 810*m*, 690*s*. EI-MS: 486 (22, $M^{+\cdot}$), 427 (47, $[M - CO_2Me]^+$), 324 (11), 265 (12), 206 (26), 145 (100, $[Ph{-}C{\equiv}N{-}CMe_2]^{+\cdot}$), 134 (23), 104 (29). Anal. calc. for $C_{24}H_{26}N_2O_5S_2$ (486.61): C 59.24, H 5.39, N 5.76, S 13.18; found: C 58.58, H 5.21, N 5.65, S 13.10.

3. *Crystal-Structure Determination of Compounds* **7a** *and* **8a** (see *Table* and *Fig. 1*)[7]. All measurements were made on a *Rigaku-AFC5R* diffractometer in the $\omega/2\theta$-scan mode using graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å) and a 12-kW rotating anode generator. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Data collection and refinement parameters are listed in the *Table*, views of the molecules are shown in *Fig. 1*. The structures were solved by direct methods using SHELXS86 [29], which revealed the positions of all non-H-atoms. In the case of **7a**, there are two independent molecules in the asymmetric

Table. *Crystallographic Data of* **7a** *and* **8a**

	7a	**8a**
Crystallized from	EtOH	EtOH
Empirical formula	$C_{32}H_{30}N_2S_2$	$C_{32}H_{30}N_2S_2$
M_r	506.72	506.72
Crystal color, habit	colorless, prism	colorless, prism
Crystal dimensions [mm]	$0.18 \times 0.35 \times 0.44$	$0.23 \times 0.28 \times 0.47$
Temperature [K]	173(1)	173(1)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Z	4	4
Reflections for cell determination	25	25
2θ Range for cell determination [°]	37–40	24–26
Unit cell parameters a [Å]	14.124(2)	14.073(3)
b [Å]	16.363(2)	9.378(3)
c [Å]	11.676(2)	21.664(3)
α [°]	90.74(1)	90
β [°]	103.29(1)	105.78(1)
γ [°]	96.12(1)	90
V [Å^3]	2609.4(6)	2751(1)
D_x [g cm^{-3}]	1.290	1.220
μ(MoK_α) [mm^{-1}]	0.228	0.216
$2\theta_{(max)}$ [°]	55	55
Total reflections measured	12452	6989
Symmetry independent reflections	11968	6326
Reflections used [$I > 2\sigma(I)$]	8457	4471
Parameters refined	889	445
Final R	0.0418	0.0422
wR ($w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$)	0.0385	0.0384
Goodness of fit	1.484	1.563
Final Δ_{max}/σ	0.0006	0.0005
$\Delta\rho$ (max; min) [e Å^{-3}]	0.31; −0.27	0.27; −0.22
Range of $\sigma(d(C{-}C))$ [Å]	0.003–0.004	0.003–0.005

[7]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-100927. Copies of the data can be obtained, free of charge, on application to the CCD, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: + 44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group using the MISSYM routine [30] of the program PLATON [31], but none could be found. The non-H-atoms were refined anisotropically. All of the H-atoms of **7a** and **8a** were located in difference electron density maps, and their positions were allowed to refine together with individual isotropic displacement parameters. All refinements were carried out on F using full-matrix least-squares procedures. Corrections for secondary extinction were not applied. Neutral-atom scattering factors for non-H-atoms were taken from [32a] and the scattering factors for H-atoms from [33]. Anomalous dispersion effects were included in F_{calc} [34]; the values for f' and f'' were those of [32b]. All calculations were performed using the TEXSAN crystallographic software package [35].

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