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Preparation and Spectroscopic Characterization of *N,N'*-Persubstituted Bis(2-Amino-5-Thienyl)Thioketones and some of their Aza Analogues

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PREPARATION AND SPECTROSCOPIC CHARACTERIZATION OF *N,N'*-PERSUBSTITUTED BIS(2-AMINO-5-THIENYL)THIOKETONES AND SOME OF THEIR AZA ANALOGUES

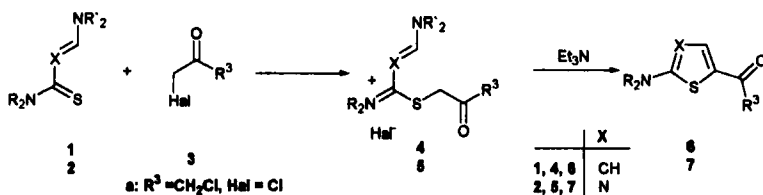
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By reaction of *N,N'*-persubstituted bis(2-amino-5-thienyl)ketones **10** and their thiazole analogues **11** and **12** with P_2S_5 hitherto unknown 2-aminothienyl- or 2-aminothiazolyl-substituted thioketones **13–15** have been prepared and characterized as strongly solvatochromic compounds their sensitivity towards the polarity or solvents is significantly higher than the one of their corresponding ketone precursors **10–12**.

Keywords: Solvent effects; thioketones; UV-Vis spectra

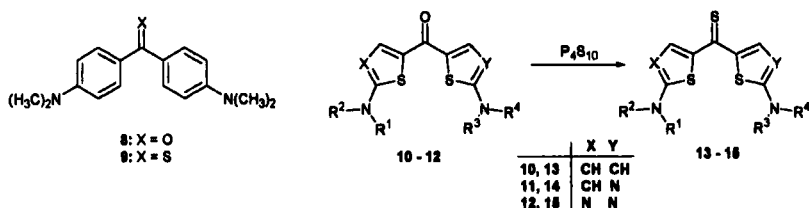
N,N'-Persubstituted 3-aminothioacrylamides **1** and their aza analogues **2** are versatile building blocks in organic chemistry.¹ They can be simply prepared by a variety of methods² and easily converted, *inter alia*, into different types of heterocycles. Thus, by reaction with halomethyl ketones **3** they can be converted into the corresponding 1-acylmethylthio-substituted vinamidinium salts **4** or their aza analogues **5** from which the 5-acyl-substituted 2-aminothiophenes **6** or 2-aminothiazoles **7**, resp., are available by reaction with bases, such as triethylamine (see Scheme 1).³



SCHEME 1

Dedicated to Prof. Dr. Juergen Fabian on the occasion of his 65th birthday.
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Recently, it was demonstrated that the 3-aminosubstituted thioacrylamides **1** and their aza analogues **2**⁴ are able to react with 1,3-dichloroacetone (**3a**, $R^3 = CH_2Cl$, $Hal = Cl$) to yield the hitherto unknown *N,N'*-persubstituted bis(2-aminothienyl)ketones **10** and their aza analogues **11** and **12**.⁵ These ketones are heterocyclic analogues of the well-known Michlers Ketone **8**⁶ and, like this compound and its thio derivative **9**, able to be used as educts for the preparation of different types of dyes. For instance, the ketones **10–12** have been used as starting materials in the preparation of heterocyclic Crystal Violet analogues. Now we have found that the heterocyclic ketones **10–12** can be converted in analogy to the transformation of Michlers Ketone **8** into its thio derivative **9**,⁷ into the heterocyclic thioketone derivatives **13–15** by reaction with P_4S_{10} . Satisfactory yields could be obtained when the mentioned compounds were allowed to react in pyridine at elevated temperatures (see Scheme 2).



SCHEME 2

The thioketones **13–15** so prepared are deeply coloured compounds. Their structures have been confirmed by means of elemental analysis and several spectroscopic methods. Thus, in the mass spectra intense molecular ion peaks were found. Moreover, characteristic fragment peaks were observed for the morpholino derivatives at ($M^+ - 86$) and for the diphenylamino derivatives at ($M^+ - 168$). These peaks can be attributed to fragments which were formed by elimination of a morpholino or diphenylamino moiety, resp., from the corresponding molecular ions. In the mass spectra of the thiazole derivatives **14** and **15** further peaks with moderate intensity were found. These peaks are originated from the elimination of corresponding *N,N*-disubstituted cyanamide moieties.

In the IR spectra of the thioketones **13–15**, contrary to the corresponding ketones **10–12** which exhibit intense bands at about 1700 cm^{-1} originating from their carbonyl moiety, no bands in this spectral region could be detected demonstrating the absence of a carbonyl group in these compounds.

In the ^{13}C NMR spectra of the thioketones **13–15** the presence of a thiocarbonyl moiety is indicated by a signal at about 190 ppm.

Due to their deep color the thioketones exhibit in their UV/Vis spectra intense absorptions at about 500 nm whose positions depend significantly on their substitution pattern as well as on the polarity of the solvents applied. Thus, the diphenylamino-substituted thioketones absorb at significantly longer wavelengths than their morpholino derivatives and the thienyl-substituted ketones **13** and **14** absorb at longer wavelength than the bis(thiazolyl)ketones **15**. In analogy to other 5-acceptor substituted 2-aminothiophene and 2-aminothiazole derivatives⁸ the solvent induced shift of the absorption maxima, measured in 10^5 cm^{-1} , correlates linearly with the solvent polarity parameter π^* introduced by Kamlet and Taft⁹ according to eq. (1):

$$1/\lambda = a + b \cdot \pi^* \quad (1)$$

This follows from the data depicted in Table I in which, besides the absorption wavelengths of the thioketones as function of solvents, the a and b values of equation (1) and the corresponding correlation coefficients r are summarized. The negative signs of the second terms b in equation (1) indicate for all compounds a positive solvatochromism which decreases in the sequence **13** > **14** > **15**. The highest b -values were found in each series for the morpholino derivatives. The positive b -values of the thioketone derivatives **13–15** exceed those of the corresponding ketone derivatives **10–12** which exhibit, in general, a significantly lower solvatochromism with lower correlation coefficients (Table I).

EXPERIMENTAL

Melting points were determined by means of a Boetius heating-table microscope. The IR spectra were recorded in potassium bromide pellets with a Philips 9624 FTIR spectrometer PU 9624, the UV/VIS absorption spectra with a Perkin-Elmer spectrometer Lambda 900, the NMR spectra with a Varian 300 MHz spectrometer Gemini 300, and the mass spectra with a spectrometer AMD 402. The elemental analyses were estimated by means of a LECO analyser CHNS 932.

Preparation of the Thioketones **13–15** (General Procedure)

P_4S_{10} (0.01 mol, 4.4 g) and pyridine (50 ml) were mixed and refluxed for 1 h. After cooling the reaction mixture a heterocyclic ketone (0.01 mol)

TABLE I Solvatochromic Data of the Heterocyclic Thioketones 13–15 and Some of Their Carbonyl Analogues 10–12

Nr.	R ¹ R ² N ^a	Solvent: CH		X _b	TE	DN	TO	ET	AN	MC	DMF	DMSO	lgε ^b	a	b	r
		π*	CH		+0.02	+0.26	+0.52	+0.53	+0.78	+0.78	+0.78	+1.01				
13a	Morpholino		474	CH	488	505	497	509	514	511	519	530	4.62	21.03	-2.09	-0.98 ⁴
13b	Diphenylamino		509	CH	521	528	526	530	537	539	541	547	4.62	19.61	-1.31	-0.9929
13c	Methylamino		493	CH	505	508	512	530	530	531	534	545	4.51	20.32	-1.90	-0.9465
13d	Dimethylamino		486	CH	498	510	506	534	520	525	531	544	4.15	20.56	-2.07	-0.9242
14a	Morpholino		462	N	477	515	488	499	501	500	506	515	4.50	21.37	-2.03	-0.8725
15a	Morpholino		444	N	453	471	462	459	472	468	478	483	4.48	22.50	-1.72	-0.9459
15b	Diphenylamino		466	N	471	476	479	474	482	482	488	491	4.60	21.51	-1.07	-0.9644
10a	Morpholino		405	CH	394	408	403	425	416	414	419	424	4.60	25.10	-1.39	-0.7159
11a	Morpholino		394	N	387	406	397	416	405	401	407	414	4.51	25.57	-1.28	-0.6957
12a	Morpholino		—	N	373	379	379	385	382	382	387	391	4.43	27.13	-1.48	-0.9179

CH: cyclohexane; TE: tetrachloromethane; DN: dioxane; TO: toluene; ET: ethanol; AN: acetonitrile; MC: dichloromethane; DMF: dimethylformamide; DMSO: dimethyl sulphoxide.

^aR¹/R² = R³R⁴

^bEstimated in MC.

was added under stirring. Then, the mixture is refluxed a second time until all starting material was, according to a TLC analysis, vanished. After cooling the reaction mixture was diluted with water and the product precipitated was isolated by filtration. After drying the product obtained was recrystallized from DMF.

The following thioketones have been prepared in this manner:

Bis(2-morpholino-5-thienyl)thioketone 13a, yield 72%; mp. 238–240°C. ^1H NMR (CDCl_3): δ = 3.30 (t, 8H, CH_2), 3.80 (t, 8H, CH_2), 6.12 (d, 2H, CH), 7.37 (d, 2H, CH); ^{13}C NMR (CDCl_3): δ = 49.46, 65.87, 105.88, 131.59, 138.11, 168.52, 194.29. –MS (70 eV); m/z (%): 380 [M^+] (100), 347 (12), 294 (16), 269 (5). $-\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_3$ (380.52): calcd. C 53.66 H 5.30 N 7.36 S 25.28; found C 52.95 H 5.31 N 7.03 S 25.31.

Bis(2-diphenylamino-5-thienyl)thioketone 13b, yield 58%; mp. 174–175°C. ^1H NMR (CDCl_3): δ = 6.38 (d, 2H, CH), 7.18 (t, 4H, CH), 7.24–7.36 (m, 18H, CH); ^{13}C NMR (CDCl_3): δ = 113.81, 125.44, 125.96, 129.73, 130.86, 140.48, 145.92, 164.83, 195.71. –MS (70 eV); m/z (%): 544 [M^+] (100), 376 (28), 294 (20), 167 (18), 77 (75). $-\text{C}_{33}\text{H}_{24}\text{N}_2\text{S}_3$ (544.74): calcd. C 72.76 H 4.44 N 5.14 S 17.66; found C 72.49 H 4.74 N 4.86 S 17.87.

Bis[2-(N-methylanilino)-5-thienyl]thioketone 13c, yield 83%; mp. 154–156°C. ^1H NMR (CDCl_3): δ = 3.45 (s, 6H, CH_3), 6.14 (d, 2H, CH), 7.24 (t, 2H, CH), 7.31–7.43 (m, 10H, CH); ^{13}C NMR (CDCl_3): δ = 42.70, 108.22, 124.66, 126.53, 129.96, 131.83, 138.22, 146.53, 167.03, 192.76. –MS (70 eV); m/z (%): 420 [M^+] (100), 314 (12), 232 (8), 188 (11). $-\text{C}_{23}\text{H}_{20}\text{N}_2\text{S}_3$ (420.60): calcd. C 65.68 H 4.79 N 6.66 S 22.87; found C 65.63 H 4.81 N 6.38 S 22.48.

Bis(2-dimethylamino-5-thienyl)thioketone 13d, yield 48%; mp. 178–180°C. ^1H NMR (CDCl_3): δ = 3.05 (s, 12H, CH_3) 5.95 (d, 2H, CH), 7.37 (d, 2H, CH); ^{13}C NMR (CDCl_3): δ = 41.95, 104.86, 132.40, 136.55, 168.69, 190.19. –MS (70 eV); m/z (%): 296 [M^+] (100), 263 (13), 252 (18), 169 (15) 126 (23), 64 (22). $-\text{C}_{13}\text{H}_{16}\text{N}_2\text{S}_3$ (296.46): calcd. C 52.67 H 5.44 N 9.45 S 32.44; found C 52.52 H 5.68 N 9.10 S 32.37.

(2-Morpholino-5-thienyl)-(2-morpholino-5-thiazolyl)thioketone 14a, yield 96%; mp. 255–257°C. ^1H NMR (CDCl_3): δ = 3.36 (t, 4H, CH_2), 3.59 (t, 4H, CH_2), 3.78 (t, 8H, CH_2), 6.17 (d, 1H, CH), 7.44 (d, 1H, CH), 7.61 (s, 1H, CH). ^{13}C NMR (CDCl_3): δ = 48.40, 49.48, 65.86, 66.02, 106.62, 132.67, 138.15, 138.24, 139.55, 170.47, 174.34, 193.34. –MS (70 eV); m/z (%): 381 [M^+] (100), 348 (8), 295 (20), 269 (48), 212 (22), 205 (27). $-\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_2\text{S}_3$ (381.51): calcd. C 50.37 H 5.02 N 11.01 S 25.21; found C 50.32 H 5.34 N 11.04 S 25.61.

Bis(2-morpholino-5-thiazolyl)thioketone 15a, yield 86%; mp. 260–262°C. ^1H NMR (CDCl_3): δ = 3.63 (t, 8H, CH_2), 3.79 (t, 8H, CH_2), 7.72 (s, 2H, CH). ^{13}C NMR (CDCl_3): δ = 48.44, 65.93, 138.59, 140.97,

175.16, 194.78. —MS (70 eV); m/z (%): 382 [M⁺] (100), 325 (18), 270 (35), 213 (22) 206 (20). —C₁₅H₁₈N₄O₂S₃ (382.50): calcd. C 47.10 H 4.74 N 14.65 S 25.15; found C 46.77 H 4.78 N 14.43 S 25.98.

Bis(2-diphenylamino-5-thiazolyl)thioiketone 15b, yield 68%; mp. 210–212°C. —¹H NMR (CDCl₃): δ = 7.30–7.33 (m, 4H, CH), 7.37–7.42 (m, 16H, CH), 7.79 (s, 2H, CH); ¹³C NMR (CDCl₃): δ = 126.37, 127.60, 129.94, 140.17, 141.17, 143.62, 174.98, 196.19. —MS (70 eV); m/z (%): 546 [M⁺] (100), 378 (10), 352 (18), 295 (28), 167 (33), 104 (15), 77 (60). —C₃₁H₂₂N₄S₃ (546.72): calcd. C 68.10 H 4.06 N 10.25 S 17.59; found C 68.13 H 4.56 N 9.65 S 17.63.

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