Monatshefte für Chemie 120, 561—569 (1989)

Monatshefte für Chemie
Chemical Monthly

On the Reaction of Dithiocarbamates with Nitrogen-Containing Derivates of Oxalic Acid

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Summary. The action of bisimidochlorides of oxalic acid on dithiocarbamates produces 2-thioxo-3-aryl(alkyl)-4,5-diiminothiazolidines by cycloacylation. The molecular structure of 2-thioxo-3-(4-methoxyphenyl)-4,5-bis(phenylimino)-thiazolidine is confirmed by X-ray crystal structure analysis.

Keywords. Derivatives of oxalic acid; Dithiocarbamates; MNDO-Calculation; NS-Heterocycles; X-ray diffraction.

Zur Reaktion von Dithiocarbaminaten mit stickstoffhaltigen Derivaten der Oxalsäure

Zusammenfassung. Bei der Einwirkung von Bisimidchloriden der Oxalsäure auf Dithiocarbaminate entstehen durch Cycloacylierung 2-Thioxo-3-aryl(alkyl)-4,5-diiminothiazolidine. Die Molekülstruktur von 2-Thioxo-3-(4-methoxyphenyl)-4,5-bis(phenylimino)thiazolidin wird durch Röntgenkristallstrukturanalyse bestätigt.

Introduction

Dithiocarbamates (easily available from primary and secondary amines and CS_2) are versatile intermediates of the chemical industry. Because of pronounced fungicide properties these compounds have attracted particular interest. Formerly studied reactions of dithiocarbamates with oxalyl chloride resulted, in general, in rearrangement of the primarily generated products of cycloacylation [1].

This study aims at investigating the behaviour of dithiocarbamates towards bisimidchlorides. The structure of one of the products obtained has been determined by X-ray diffraction.

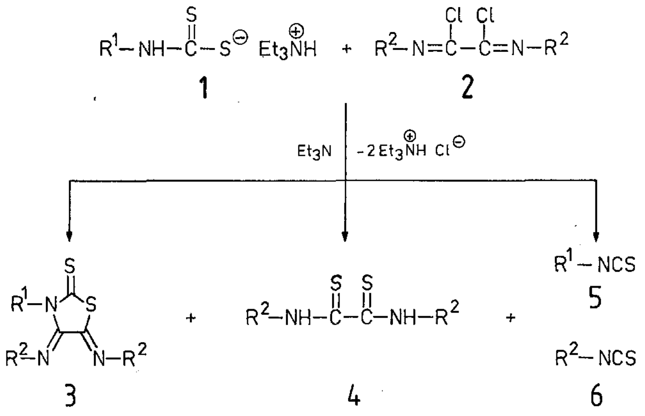
Results and Discussion

Reaction of Bisimidchlorides with Dithiocarbamates

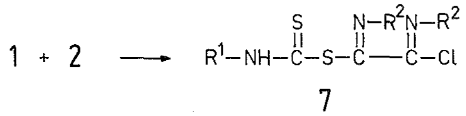
Because of their poor solubility, the alkali salts of the dithiocarbamates were replaced by the triethylammonium salts (**1**). In all cases studied the reaction of **1** with bisimidchloride (**2**) proceeded slightly exothermic and the colour of the reaction mixture turned to red. The reaction is completed after about 15 minutes. The products of the cycloacylation (**3**), which are obtained with different yields, can easily be purified by recrystallisation. The colour of them varies from yellow to red.

By -products of these reactions are isothiocyanates (**5**, **6**) as well as dithiooxalamides (**4**). Without doubt, isothiocyanates result from acylation of **1** and subsequent fragmentation of **7**.

The formation of **7** accounts for the fact that a heterocumulene can be generated both from dithiocarbamate **1** and from the corresponding bisimidchloride **2**. If R^1 = 4-$MeOC_6H_4$ and R^2 = C_6H_5 the presence of both products (4-methoxyphenylisothiocyanate and phenylisothiocyanate) has been established by GC. Small quantities of dithiooxamides might be formed by nucleophilic thiolation of bisimidchloride (perhaps via **7**).



1	2	3	R^1	R^2
a	a	a	β–$C_{10}H_7$	C_6H_5
b	a	b	4-FC_6H_4	C_6H_5
c	a	c	4-ClC_6H_4	C_6H_5
d	a	d	4-BrC_6H_4	C_6H_5
e	a	e	C_6H_5	C_6H_5
f	a	f	4-$CH_3OC_6H_4$	C_6H_5
g	a	g	4-$C_2H_5OC_6H_4$	C_6H_5
h	a	h	4-$CH_3C_6H_4$	C_6H_5
i	a	i	$C_6H_5CH_2$	C_6H_5
j	a	j	4-$(CH_3)_2NC_6H_4$	C_6H_5
f	b	k	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$
e	b	l	C_6H_5	4-$CH_3OC_6H_4$
b	c	m	4-FC_6H_4	4-$C_2H_5OOCC_6H_4$
g	c	n	4-$C_2H_5OC_6H_4$	4-$C_2H_5OOCC_6H_4$
k	d	o	$(CH_3)_2N-(CH_2)_3$	4-$CH_3C_6H_4$
k	d	p	$(CH_3)_3\overset{+}{N}-(CH_2)_3$	4-$CH_3C_6H_4$
k	d	r	$(CH_3)_3\overset{+}{N}-(CH_2)_3$	4-$CH_3C_6H_4$



$$1 + 2 \longrightarrow R^1-NH-\overset{S}{\overset{\|}{C}}-S-\overset{N-R^2}{\overset{\|}{C}}-\overset{N-R^2}{\overset{\|}{C}}-Cl$$

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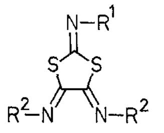
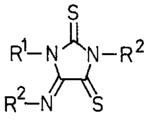
The compounds of the series **3** display a positive Feigl-test. Consequently, they possess at least one thiocarbonyl group. This could be confirmed by ^{13}C NMR spectroscopy. Strongly downfield-shifted signals (190–193 ppm) indicate the thiocarbonyl group. In addition, the non-symmetry of the molecule is reflected in the NMR spectrum.

Probably, the compounds **3** are formed via the intermediates **8**, which undergo a rapid Dimroth-type rearrangement. The isolation of **8** (R^1 = 4-$Me_2NC_6H_4$, R^2 = C_6H_5, yield 5%) in one case may be considered as an indication for such a mechanism. All attempts failed, however, to detect **8** in the course of the reaction.



8



9

According to ^{13}C NMR and UV spectra dithio-derivatives of the type **9** are not produced. They are also not accessible from **3** or **8** by treatment with *tert.* amines and trifluoro acetic acid.

Final evidence for the structural assignment is furnished by the X-ray diffraction analysis of **3** (R^1 = 4-MeOC_6H_4, R^2 = C_6H_5).

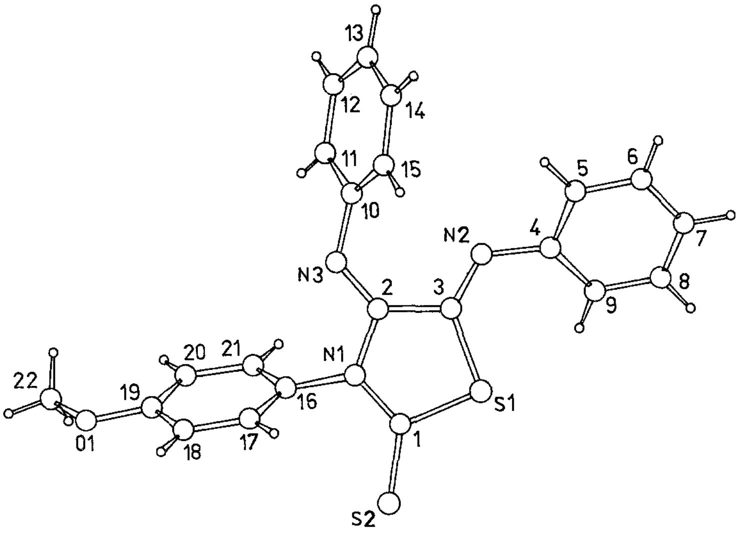


Fig. 1. A perspective view of the molecule **3f** showing atomic numbering. The base numbers are for the carbon atoms unless indicated otherwise. The H-atoms are shown but not labelled

Molecular Structure of 2-Thioxo-3-(4-methoxyphenyl)-4,5-bis(phenylimino)-thiazolidine (**3f**)

The molecular geometry depicted in Fig. 1 is computed from the final fractional atomic coordinates listed in Tables 1 and 2. Bond distances and angles are given in Table 3.

The planar heterocyclic thiazolidine ring is formed by five multiple bonds. Due to the difference in their neighborhood the S(II)—C(sp^2) distances, differ slightly: 1.775(2) vs. 1.758(2) Å. In accordance with the planarity of the central ring the substituents atoms S(2), N(2), N(3) and C(16) lie practically in its best plane. S(2), N(2) and N(3) maintain strong double bonds with the central ring as shown by the corresponding CX bond lengths: 1.625(2), 1.260(2) and 1.271(2), respectively. The two phenylimino moieties exhibit identical C_{ph}—N(sp^2) distances of 1.412(2) Å, somewhat shorter than the CN distance pertaining to the N(1)-phenyl group. It is worth mentioning that **3f** has five different types of C—N bonds as listed in Table 4.

Table 1. Relative fractioned atomic coordinates of **3f** for nonhydrogen atoms with e.s.d.s in parentheses. Anisotropic thermal parameters are deposited at the Cambridge Crystallographic Center, University Chemical Laboratory, Cambridge, Lensfied Road, CB 2 IEW

Atom	x/a	y/b	z/c
S(1)	0.60291 (5)	0.10958 (5)	0.06615 (2)
S(2)	0.84155 (5)	0.07041 (6)	− 0.00034 (3)
O(1)	0.8288 (1)	0.3714 (1)	− 0.28562 (6)
N(1)	0.6287 (1)	0.2152 (1)	− 0.05010 (7)
N(2)	0.3732 (1)	0.2590 (1)	0.05344 (7)
N(3)	0.4355 (1)	0.3296 (1)	− 0.08413 (7)
C(1)	0.6955 (1)	0.1350 (1)	− 0.00138 (9)
C(2)	0.5032 (1)	0.2610 (1)	− 0.03824 (9)
C(3)	0.4748 (1)	0.2180 (1)	0.03007 (9)
C(4)	0.3360 (1)	0.2245 (1)	0.11719 (9)
C(5)	0.2019 (1)	0.2133 (2)	0.11977 (9)
C(6)	0.1557 (2)	0.1822 (2)	0.1799 (1)
C(7)	0.2421 (2)	0.1654 (2)	0.2381 (1)
C(8)	0.3744 (2)	0.1802 (2)	0.2365 (1)
C(9)	0.4228 (2)	0.2095 (2)	0.17661 (9)
C(10)	0.3079 (1)	0.3810 (1)	− 0.08092 (8)
C(11)	0.2897 (1)	0.5178 (2)	− 0.0912 (1)
C(12)	0.1669 (2)	0.5739 (2)	− 0.0925 (1)
C(13)	0.0605 (2)	0.4935 (2)	− 0.0859 (1)
C(14)	0.0762 (2)	0.3563 (2)	− 0.0791 (1)
C(15)	0.1997 (1)	0.2996 (2)	− 0.07610 (9)
C(16)	0.6832 (1)	0.2567 (1)	− 0.11024 (9)
C(17)	0.7071 (2)	0.1629 (2)	− 0.1589 (1)
C(18)	0.7564 (2)	0.2048 (2)	− 0.2165 (1)
C(19)	0.7795 (1)	0.3403 (2)	− 0.22670 (9)
C(20)	0.7531 (1)	0.4342 (2)	− 0.17903 (9)
C(21)	0.7059 (1)	0.3919 (1)	− 0.12025 (9)
C(22)	0.8534 (2)	0.5095 (2)	− 0.2981 (1)

Table 2. Relative fractional atomic coordinates of **3f** for H-atoms with e.s.d.s in parentheses

Atom	*x/a*	*y/b*	*z/c*
H(5)	0.143(1)	0.224(1)	0.0778(8)
H(6)	0.063(1)	0.173(2)	0.1800(9)
H(7)	0.211(1)	0.144(2)	0.280(1)
H(8)	0.433(1)	0.169(2)	0.2758(9)
H(9)	0.515(1)	0.223(2)	0.1762(9)
H(11)	0.363(1)	0.571(2)	− 0.0977(9)
H(12)	0.155(1)	0.668(2)	− 0.0989(9)
H(13)	− 0.027(1)	0.529(2)	− 0.086(1)
H(14)	0.001(1)	0.301(2)	− 0.0762(9)
H(15)	0.211(1)	0.206(1)	− 0.0714(9)
H(17)	0.690(1)	0.071(2)	− 0.1509(9)
H(18)	0.776(1)	0.141(2)	− 0.249(1)
H(20)	0.769(1)	0.527(1)	− 0.1862(9)
H(21)	0.689(1)	0.455(2)	− 0.0860(9)
H(22a)	0.891(2)	0.513(2)	− 0.337(1)
H(22b)	0.775(2)	0.563(2)	− 0.300(1)
H(22c)	0.919(2)	0.547(2)	− 0.262(1)

For a better comparison the bond orders—computed by the modified Coulson formula [2, 3]—are also presented. The dihedral angles of N(2)-phenyl and N(3)-phenyl rings to that of the central thiazolidine moiety 33.0(1)° vs. 56.8(4)° show that their orientation has no visible effect upon the strength of the N(sp^2)-phenyl bonds. The dihedral angle of the best planes of these two phenyl rings is 71.9(4)°. The third phenyl ring with a 4-methoxy substituent makes a dihedral angle of 62.3(1)° with that of the thiazolidine ring. An analysis of the intramolecular non-bonded distances and the corresponding torsion angles has shown that there is no strong hydrogen bond of the type $NH \cdots X$ ($X = $ S or N).

The experimental geometry of **3f** is well reproduced by the MNDO calculation [4]. This calculation was fully geometry-optimized with respect to all internal coordinates. Apart from the CS-bond lengths, which according to [5] are in general overestimated by 0.06 Å, the calculated bond lengths deviate from the experimental data within the range of formerly found mean absolute errors [4]. The calculated bond lengths, bond angles and dihedral angles are summarized in Table 4. The calculated MNDO π-bond orders of the CN bonds follow closely those estimated from experiment by means of the relationship derived by Coulson. Molecular distortion is in general overestimated within the MNDO approximation [5]. In the case of **3f** two of the phenyl groups are completely rotated out of the plane. Interestingly, the (N)2-phenyl group behaves different. As found in the X-ray study this group is less tilted than the other ones. This suggests that the difference in rotation of the two N-phenyl groups is due to intramolecular rather than crystal forces.

Experimental

The melting points are uncorrected. The UV spectra were recorded on a Carl-Zeiss-Jena UV/VIS-

Table 3. Bond lengths and angles of **3f** with e.s.d.s in parentheses

Bond lengths (Ångstrom) with e.s.d.s

S1	–C1	1.758(2)	N3	–C2	1.271(2)	C10	–C15	1.384(3)
S1	–C3	1.775(2)	N3	–C10	1.412(2)	C11	–C12	1.373(3)
S2	–C1	1.625(2)	C2	–C3	1.488(3)	C12	–C13	1.369(3)
O1	–C19	1.369(2)	C4	–C5	1.386(2)	C13	–C14	1.372(4)
O1	–C22	1.417(3)	C4	–C9	1.394(3)	C14	–C15	1.379(3)
N1	–C1	1.367(2)	C5	–C6	1.376(3)	C16	–C17	1.385(3)
N1	–C2	1.411(2)	C6	–C7	1.376(3)	C16	–C21	1.376(3)
N1	–C16	1.443(2)	C7	–C8	1.368(3)	C17	–C18	1.374(3)
N2	–C3	1.260(2)	C8	–C9	1.378(3)	C18	–C19	1.381(3)
N2	–C4	1.412(2)	C10	–C11	1.377(3)	C19	–C20	1.379(3)
						C20	–C21	1.386(3)

Bond angles (deg.) with e.s.d.s

C1	–S1	–C3	92.7(1)	C6	–C7	–C8	120.1(3)
C19	–O1	–C22	117.3(3)	C7	–C8	–C9	120.6(4)
C1	–N1	–C2	116.9(3)	C4	–C9	–C8	119.7(3)
C1	–N1	–C16	122.8(3)	N3	–C10	–C11	117.2(3)
C2	–N1	–C16	120.2(2)	N3	–C10	–C15	123.2(3)
C3	–N2	–C4	125.7(3)	C11	–C10	–C15	119.2(3)
C2	–N3	–C10	125.8(3)	C10	–C11	–C12	120.5(3)
S1	–C1	–S2	121.3(2)	C11	–C12	–C13	120.1(4)
S1	–C1	–N1	110.8(2)	C12	–C13	–C14	120.0(4)
S2	–C1	–N1	127.9(2)	C13	–C14	–C15	120.1(3)
N1	–C2	–N3	118.6(3)	C10	–C15	–C14	120.0(3)
N1	–C2	–C3	110.4(3)	N1	–C16	–C17	120.6(3)
N3	–C2	–C3	131.0(3)	N1	–C16	–C21	119.1(3)
S1	–C3	–N2	130.5(2)	C17	–C16	–C21	120.2(3)
S1	–C3	–C2	108.8(2)	C16	–C17	–C18	119.8(3)
N2	–C3	–C2	120.7(3)	C17	–C18	–C19	120.2(3)
N2	–C4	–C5	115.7(3)	O1	–C19	–C18	115.6(3)
N2	–C4	–C9	124.9(3)	O1	–C19	–C20	124.3(3)
C5	–C4	–C9	119.3(3)	C18	–C19	–C20	120.1(3)
C4	–C5	–C6	120.1(3)	C19	–C20	–C21	119.8(3)
C5	–C6	–C7	120.2(3)	C16	–C21	–C20	120.0(3)

Specord spectrometer, and the ^{13}C NMR spectra were recorded on a Bruker FT nuclear resonance spectrometer WH-90. The NMR data are reported in (ppm) relative to internal tetramethylsilane ($\delta = 0$). Elemental analyses were obtained by an automatic micro procedure.

X-ray Analysis

A crystal with dimensions of $0.11 \times 0.19 \times 0.40$ mm was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. Cell dimensions were obtained by least-squares from the setting angles of 25 carefully centered reflections whose approximate positions had previously been obtained from a random peak search. The monoclinic symmetry was established by the systematic absences in $h0l\; l = 2n + 1$ and in $0k0\; k = 2n + 1$. Intensities of all reflections within

Table 4. Experimental and theoretical C—H bond lengths of **3f** and π-bond orders

Bond	Nature of the bond	Bond lengths[a] in Å		Bond orders[b]	
		$B_{\text{exp.}}$	$B_{\text{calc.}}^{\text{MNDO}}$	p_{π}^{C}	p_{π}^{MNDO}
C3—N2		1.260 (2)	1.285	(1.00)	0.94
C2—N3	$C(sp^2)=N_b(sp^2)$	1.271 (2)	1.288	0.86	0.91
C1—N1	$C(sp^2)—N_t(sp^2)$	1.367 (2)	1.405	0.39	0.42
C2—N1	$C(sp^2)—N_t(sp^2)$	1.411 (2)	1.436	0.21	0.31
C4—N2		1.412 (2)	1.422	0.21	0.17
C10—N3	$C_{ph}—N_b(sp^2)$	1.412 (2)	1.417	0.21	0.16
C16—N1	$C_{ph}=N_t(sp^2)$	1.443 (2)	1.440	0.09	0.14

[a] $B_{\text{exp.}}$: bond length observed; $B_{\text{calc.}}^{\text{MNDO}}$: bond length obtained by fully geometry-optimized MNDO calculations [4]. The remaining geometrical data are as follows: bond lengths in Å: S1—C1 1.704, C3—S1 1.703, C2—C3 1.503, S2—C1 1.556, C19—O1 1.361, C22—O1 1.401, C—C in the *ph*-groups (av.) 1.411, C—H of the *ph*-groups (av.) 1.091, CH of the *Me*-group (av.) 1.117, bond angles in degree: C3—S1—C1 96.3, C2—C3—S1 109.4, N1—C2—C3 108.9, S2—C1—S1 124.1, N2—C3—S1 129.7, C4—N2—C3 124.1, N3—C2—C3 134.2, C10—N3—C2 126.3, C16—N1—C2 122.4, O1—C19—C20 124.8, C22—O1—C19 123.3, bond angles C—C—C in the *ph*-groups and H—C—C at the phenyl groups (av.) 120.0, bond angles of *Me* 106.0 and 112.5, resp.; dihedral angles in degree: of C9—C4—N2—C3 79.4 and of the remaining *ph*-groups 90 ± 3, relative to the central ring; departure of the rings from planarity 0 ± 1. Heat of formation of **3f**: 463 kJ/mol

[b] p_{π}^{C}: π-bond orders calculated by the modified Coulson formula [2, 3] from $B_{\text{exp.}}$ adopting the following reference bond lengths: S (CN single bond) 1.47 Å and D (CN double bond) 1.26 Å; $B_{\text{exp.}} = S-(S-D)/[1 + 0.6625\ (1 - p^C)/p^C]$. p_{π}^{MNDO}: π-bond orders calculated within the all-valence electron approximation using the MNDO-method [4]. The π-system is defined with respect to the plane of the central ring

$3 < 2\theta < 150^\circ$ were measured in the $\omega - 2\theta$ scan mode at 296 ± 1 K using CuK$_\alpha$ ($\lambda = 1.54184$ Å) radiation. After conventional data reduction of 4308 measurements 3625 were unique and not systematically absent. As a check on crystal and electronic stability three well chosen reflections ($\bar{4}\bar{6}\bar{3}$, $\bar{6}0\bar{8}$ and $0\bar{6}5$) were measured every hour. The intensities of these standards remained constant within experimental error throughout data collection.

The structure was solved by direct methods (MULTAN 82 [6]) using 288 normalized structure factors $E \geqslant 1.46$. Twenty seven nonhydrogen atoms were located in the *E*-map computed with the best statistical parameters. The missing atom was determined by difference Fourier synthesis. At the end of the least-squares refinement of the atomic coordinates in isotropic mode an empirical absorption ($\mu = 25.0\ \text{cm}^{-1}$) correction was applied by the use of the program DIFABS [7]. Relative transmission coefficients ranged from 0.810 to 1.382 with an average of 0.991. The H-atoms were generated from assumed geometries and their positions were refined isotropically along with the anisotropic treatment for the non-H atoms. The full-matrix least-squares refinement for 254 parameters using 2980 reflections selected with the criteria $|F|^2 \geqslant 3.0\,\sigma(F^2)$ including the refinement of a secondary extinction coefficient improved R to a final 0.036 ($\omega R = 0.039$, $R_{\text{tot}} = 0.052$). The highest peak in the final difference map was 0.22 e/Å while the greatest shiftover-error was 0.24. Scattering factors were taken from standard tables [8]. The calculations have been carried out on a PDP-II/34 minicomputer in Budapest using the Enraf-Nonius SDP system with local modifications*.

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* The structure factor tables can be obtained from the authors on request

Syntheses

General Procedure for Synthesis of the Dithiocarbamates **1a** *to* **1k**

The corresponding primary amine (0.1 mol) was dissolved in 200 ml dry diethylether. After addition of 10.2 g (0.1 mol) triethylamine a solution of 7.7 g (0.1 mol) CS_2 in 50 ml diethylether was added dropwise with stirring. After a short time, the exothermic reactions result in the precipitation of a white or slightly yellow crystalline solid. The precipitate was separated, dried and immediately used, without any additional purification, as starting material for the following reactions.

Bisimidchlorides of the Oxalic Acid

Preparation as described in Ref. [9].

Bis-(4-carbethoxyphenyl)oxalimidchloride (**2c**)

Oxalic bis(4-carbethoxyphenyl)amide (77.2 g, 0.2 mol) in 500 ml toluene was refluxed with PCl_5 (83.4 g, 0.4 mol). The reaction is completed when a homogeneous yellow solution is formed (after about 4 h). Then the solution was filtered and the solvent and $POCl_3$, formed within the reaction, removed *in vacuo*. The residue was recrystallized from *n*-hexane/chloroform. Yield: 59.1 g (70%), light-yellow, m.p.: 166–168°C. $C_{20}H_{18}Cl_2N_2O_4$ (421.3); calc. C 56.97, H 4.27, N 6.65; found C 57.03, H 4.19, N 6.71.

General Procedure for Synthesis of the 2-Thioxo-3-aryl(alkyl)-4,5-bis(arylimino)thiazolidines **3a–3r**

The corresponding dithiocarbamates **1a–1k** (0.02 mol) were dissolved in 100 ml dry chloroform and the solution mixed with triethylamine (1.55 g, 0.02 mol). Then 0.02 mol of the corresponding

Table 5. Synthesized 2-thioxo-3-aryl(alkyl)-4,5-bis(arylimino)thiazolidines (**3**)

Compound	Formula[a]	(Mol. Wt.)	M.P. (°C)	Yield (%)
3a	$C_{25}H_{17}N_3S_2$	(423.6)	193–196	56
3b	$C_{21}H_{14}FN_3S_2$	(391.5)	205–208	77
3c	$C_{21}H_{14}ClN_3S_2$	(407.9)	136–140	40
3d	$C_{21}H_{14}BrN_3S_2$	(452.4)	130–131	37
3e	$C_{21}H_{15}N_3S_2$	(373.5)	173	84
3f	$C_{22}H_{17}N_3OS_2$	(403.5)	191	77
3g	$C_{23}H_{19}N_3OS_2$	(417.5)	161–164	88
3h	$C_{22}H_{17}N_3S_2$	(387.6)	133–135	62
3i	$C_{22}H_{17}N_3S_2$	(387.5)	93–96	60
3j	$C_{23}H_{20}N_4S_2$	(416.5)	227	90
3k	$C_{24}H_{21}N_3O_3S_2$	(463.6)	204–207	72
3l	$C_{23}H_{19}N_3O_2S_2$	(433.6)	205–208	71
3m	$C_{27}H_{22}FN_3O_4S_2$	(535.6)	145–147	60
3n	$C_{29}H_{27}N_3O_5S_2$	(561.7)	101–103	90
3o	$C_{22}H_{26}N_4S_2$	(410.6)	orange oil	75
3p	$C_{23}H_{29}IN_4S_2$	(552.5)	231–234	95[b]
3r	$C_{30}H_{36}N_4S_3O_3$	(596.8)	213–215	92[b]

[a] All compounds gave satisfactory analysis (C, H, N, S)

[b] From **3o** by methylation

bisimidchloride **2 a**–**2 d** was added in portions with stirring. A slightly exothermic reaction proceeds and the reaction mixture becomes intensively red. After 1 h of stirring at ambient temperature the solvent was evaporated *in vacuo*. The residue was treated with 20 ml methanol and quickly separated by filtration. The yellow to red solids were recrystallized from acetonitrile or chloroform/*n*-hexane.

Compound **3 o** is formed as orange oil. After removing the solvent it was treated with a small portion of ethanol and poured into water (1 l). The solution was extracted by diethylether. After drying **3 o** was quarternized to **3 p** and **3 r** with methyliodide and *p*-toluensulfonicmethylester, respectively, at room temperature. After standing over night the precipitated solid was collected by filtration and recrystallized from acetonitrile.

The yields melting points and spectral data of **3** are as follows:

3 e: ^{13}C NMR (22.63 MHz/$CDCl_3$): $\delta = 191.8$, 148.2, 147.6, 147.2, 146.9, 136.6, 129.4, 128.9, 128.3, 127.4, 123.5, 120.4, 119.9, 118.8 ppm.

3 f: ^{13}C NMR (22.63 MHz/$CDCl_3$): $\delta = 192.1$, 160.1, 148.3, 147.7, 147.4, 146.9, 129.9, 129.5, 128.9, 128.4, 127.4, 123.5, 120.4, 118.8, 114.8, 55.5 ppm.

3 i: ^{13}C NMR (22.63 MHz/$CDCl_3$): $\delta = 192.2$, 150.6, 148.4, 147.7, 147.4, 146.9, 129.9, 129.5, 128.9, 128.4, 127.4, 123.5, 120.4, 118.8, 112.3, 40.2 ppm. UV (chloroform) [λ in nm (lg ε)]: 268 (4.37), 326 (4.35), 356 s (4.15), 372 s (4.00), 444 s (3.34).

3 l: ^{13}C NMR (22.63 MHz/$CDCl_3$): $\delta = 191.9$, 158.8, 158.4, 156.6, 147.2, 144.2, 140.3, 137.0, 131.7, 129.4, 129.2, 129.0, 123.9, 123.5, 121.2, 114.8, 114.4, 113.6, 55.6 ppm.

3 p: ^{13}C NMR (22.63 MHz/*DMSO-d*$_6$): $\delta = 191.9$, 146.2, 145.4, 145.0, 144.0, 136.9, 132.3, 129.8, 128.4, 120.2, 119.2, 62.8, 57.3, 42.0, 20.4, 20.3 ppm.

2-(4-Dimethylaminophenyl)imino-4,5-bis(phenylimino)-1,3-dithiolane **8**

Besides **3 j** a second product was isolated from the mother liquor of the reaction of **1 j** and **2 a**. The compound **8** was obtained as dark red crystals: m.p. 153–156°C (from ethanol). UV (chloroform) [λ in nm (lg ε)]: 289 (4.07), 330 (4.07), 408 s (3.78). ^{13}C NMR (22.63 MHz/$CDCl_3$): $\delta = 158.6$, 158.0, 150.7, 150.5, 149.0, 148.4, 137.6, 129.0, 125.9, 121.6, 119.1, 112.1, 39.9 ppm. $C_{23}H_{20}N_4S_2$ (416.6); calc. C 66.35, H 4.81, N 13.46, S 15.38; found C 66.50, H 4.92, N 13.36, S 15.35.

References

[1] Stoffel P. J. (1964) J. Org. Chem. **29**: 2794

[2] Coulson C. A. (1939) Proc. R. Soc. London, Ser. A **169**: 413

[3] Liquori A. M., Vaciago A. (1956) Gazz. Chim. Ital. **86**: 769

[4] Dewar M. J. S., Thiel W. (1977) J. Amer. Chem. Soc. **99**: 4899, 4907; Dewar M. J. S., Reynolds C. H. (1956) J. Comput. Chem. **7**: 1400

[5] Fabian J., Birner P. (1988) Wiss. Z. Techn. Univ. Dresden **37**: 119, and references given therein

[6] Main P. (1982) In: Fiske S. J., Hull S. E., Lessinger L., Germain G., Declercy P.-J., Woolfson M. M. (eds.) System of Computer Programs for Automatic Solution of Crystal Structures from X-Ray Diffraction Data. University of York, Great Britain, and University of Louvain, Belgium (adapted for use on the PDP-11/34 minicomputer)

[7] Walker N., Stuart D. (1983) Acta Cryst. **A39**: 158

[8] International Tables for X-Ray Crystallography, Vol. IV (1974) Kynoch Press, Birmingham

[9] Bauer R. (1907) Ber. Dtsch. Chem. Ges. **40**: 2650; Bauer R. (1909) Ber. Dtsch. Chem. Ges. **42**: 2111

Received August 4, 1988. Accepted September 28, 1988