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SYNTHESIS AND CRYSTAL STRUCTURE OF S-(1-BENZOYL-2-BIS-METHYLTHIO)-VINYL-PIPERIDINO-DITHIOCARBAMATE

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Abstract. The S-(1-benzoyl-2-bis-methylthio)vinyl-piperidino-dithiocarbamates 2a-d are prepared by dithiocarboxylation of phenacyl-piperidino-dithiocarbamates 1a-d under phase transfer conditions followed by methylation. In dry DMF and sodium hydride the reaction of 1a-d proceeds by cyclocondensation giving the corresponding substituted 1,3-dithiole-2-thiones 5a-d after alkylation.

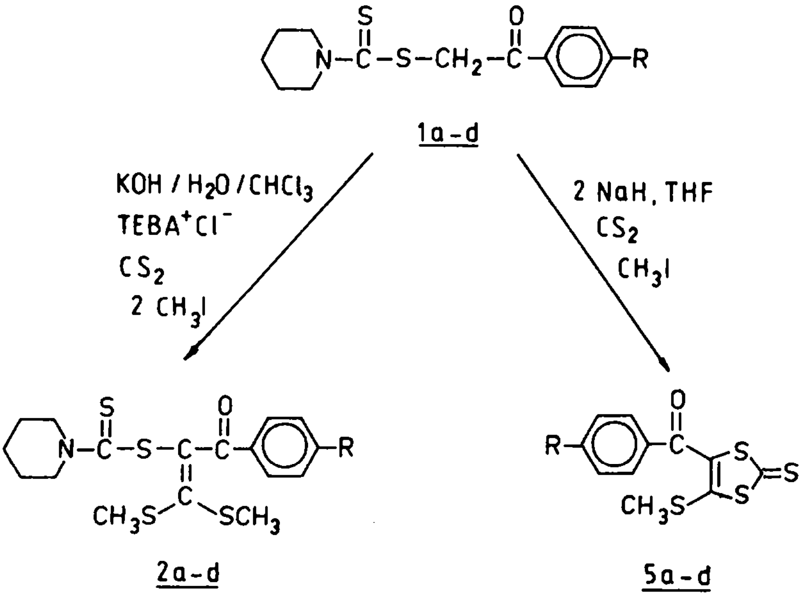
The crystal structure of the title compound has been determined by X-ray analysis. The molecules exhibit strong deviation from planarity for the α-oxoketene dithioacetal moiety by a twist of the carbonyl group out of the plane of the ethylene. The piperidino-dithiocarbamate fragment is characterized by close planarity and a short N-C bond length (1.327(4) Å) indicating substantial contribution of zwitterionic piperidinium resonance forms to the overall structure. The molecule shows a short intramolecular S...C contact distance at 3.090(3) Å between its carbonyl and thiocarbonyl group.

Synthesis

Reactions of doubly activated methylene groups with carbon disulfide and alkyl halides in the presence of a strong base (e.g. sodium hydride) are known for a long time.[1] Recently we have described the dithiocarboxylation with α-heterocarbanions of dithiocarbonate type, but this reaction proceeds by heterocyclization to 1,3-dithiole-2-thiones.[2] Following the paper of Lawesson et al.[3] concerning the reaction with CS_2 under phase transfer conditions (PTC) we have used the phenacyl-piperidino-dithiocarbamates 1a-d with the result that their α-dithiomethylene derivatives are now easily available.

In this paper we are able to report in detail that the obtained product of the dithiocarboxylation of 1 is depending on the special reaction conditions. So we have found a new convenient synthetic procedure leading to the novel compounds 2, 3 and 4, which may be considered as ethylene derivatives with three thio substituents. Compounds 2, 3 and 4 were isolated only under PTC whereas in the presence of sodium hydride the substituted 1,3-dithiole-2-thiones 5 were obtained. This fact suggests a possible mechanism based on the influence of the reaction medium on the rate of cyclization of the gem-enedithiolate as an intermediate. Our expectations have been found to be in full agreement with the experimental results.

When compound 1a (R = H) was treated with an excess of carbon disulfide at 20 - 25 °C in a two-phase system consisting of chloroform / 10% aqueous potassium hydroxide solution in the presence of an equimolar amount of triethylbenzyl ammonium chloride (TEBA chloride), 2a (R = H) was formed in 57% yield after alkylation with methyl iodide (Table 1).

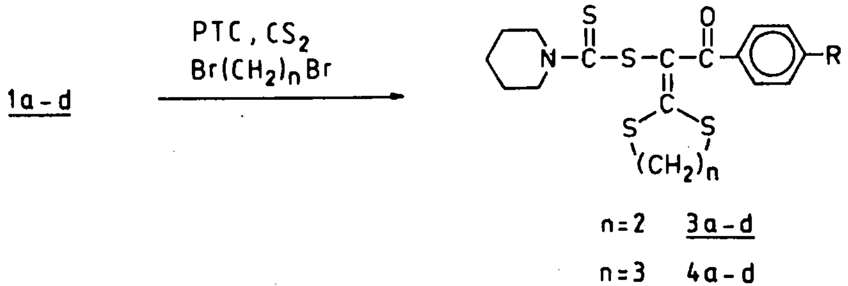


Scheme 1.

The tetraalkylammonium thiolate salts of active methylene compounds and CS_2 were reported to afford the corresponding dithio-esters and ketene dithioacetals in a 2 : 1 ratio.[3c] In our case the TEBA counter-ion is responsible for the absence of cyclization reaction. On the other hand, the thiocarbamide system in the regarded compounds is more stable. The corresponding dithiocarbonates react under phase transfer conditions with carbon disulfide in high yields to the substituted 4-alkylthio-1,3-dithiole-2-thiones.[4]

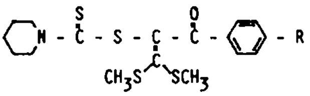
If compounds <u>1a-d</u> were treated with CS_2 in dry THF in the presence of sodium hydride no ketene dithioacetals <u>2</u> were detected. However, the 1,3-dithiole derivatives are formed after methylation in moderate yields.

In this way of phase transfer dithiocarboxylation the α-(1,3-dithiolane-2-ylidene)-phenacyl-piperidino-dithiocarbamates <u>3a-d</u> or the α-(1,3-dithiane-2-ylidene)-phenacyl-piperidino-dithiocarbamates <u>4a-d</u> are obtained using 1,2-dibromoethane and 1,3-dibromopropane, respectively, as alkylating reagent (Scheme 2, Tables 2 and 3).



Scheme 2.

Table 1.

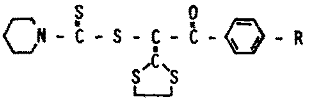


No.	R	m.p. (°C)	yield (%)	molecular formula and weight	IR $\nu_{C=O}$ (cm^{-1})	^1H-NMR ($CDCl_3$) δ (ppm)	elemental analysis calcd. / found C	H	N
<u>2a</u>	H	133 - 135	57	$C_{17}H_{21}NOS_4$ 383.62	1650	1.6 (br s, 6H, $3CH_2$) 2.18 (s, 3H, SCH_3) 2.5 (s, 3H, SCH_3) 4 (br s, 4H, $2CH_2$-N) 7.38-8.1 (m, 5H, arom.)	53.23 53.19	5.52 5.48	3.65 3.70

Table 1 cont'd...

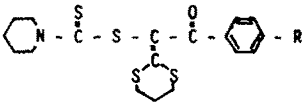
<u>2b</u>	Br	126 - 128	56	$C_{17}H_{20}NOS_4Br$ 462.52	1635	1.64 (br s, 6H, 3CH$_2$) 2.2 (s, 3H, SCH$_3$) 2.5 (s, 3H, SCH$_3$) 3.98 (br s, 4H, 2CH$_2$-N) 7.4-8.02 (m, 4H, arom.)	44.15 44.22	4.36 4.48	3.03 2.84
<u>2c</u>	Cl	131 - 132	62	$C_{17}H_{20}NOS_4Cl$ 418.11	1650	1.63 (br s, 6H, 3CH$_2$) 2.19 (s, 3H, SCH$_3$) 2.5 (s, 3H, SCH$_3$) 3.8 (br s, 4H, 2CH$_2$-N) 7.28-8.1 (m, 4H, arom.)	48.83 48.87	4.82 4.81	3.35 3.17
<u>2d</u>	CH$_3$	112 - 113	45	$C_{18}H_{23}NOS_4$ 397.65	1650	1.68 (br s, 6H, 3CH$_2$) 2.25 (s, 3H, SCH$_3$) 2.4 (s, 3H, CH$_3$-arom.) 2.52 (s, 3H, SCH$_3$) 4.1 (br s, 4H, 2CH$_2$-N) 7.15-8.1 (m, 4H, arom.)	54.37 54.71	5.83 5.89	3.52 3.45

Table 2.



No.	R	m.p. (°C)	yield (%)	molecular formula and weight	IR $\nu_{C=O}$ (cm^{-1})	^{1}H-NMR (CDCl$_3$) δ (ppm)	elemental analysis calcd. / found C	H	N
<u>3a</u>	H	180 - 182	47	$C_{17}H_{19}NOS_4$ 381.60	1620	1.5 (br s, 6H, 3CH$_2$) 3.24-3.66 (m, 4H, 2CH$_2$) 3.9 (br s, 4H, 2CH$_2$-N) 7.2-7.52 (m, 5H, arom.)	53.51 53.42	5.02 5.11	3.67 3.28
<u>3b</u>	Br	204 - 206	47	$C_{17}H_{18}NOS_4Br$ 460.50	1600	1.55 (br s, 6H, 3CH$_2$) 3.25-3.75 (m, 4H, 2CH$_2$) 3.98 (br s, 4H, 2CH$_2$-N) 7.25-7.6 (m, 4H, arom.)	44.34 44.10	3.94 3.97	3.04 2.57
<u>3c</u>	Cl	210 - 211	57	$C_{17}H_{18}NOS_4Cl$ 416.10	1600	1.58 (br s, 6H, 3CH$_2$) 3.36-3.72 (m, 4H, 2CH$_2$) 4.1 (br s, 4H, 2CH$_2$-N) 7.25-7.69 (m, 4H, arom.)	49.07 48.91	4.36 4.40	3.37 2.95
<u>3d</u>	CH$_3$	163 - 165	40	$C_{18}H_{21}NOS_4$ 395.63	1600	1.6 (br s, 6H, 3CH$_2$) 2.38 (s, 3H, CH$_3$-arom.) 3.28-3.75 (m, 4H, 2CH$_2$) 3.9 (br s, 4H, 2CH$_2$-N) 7.05-7.65 (m, 4H, arom.)	54.65 54.52	5.35 5.36	3.54 3.50

Table 3.



No.	R	m.p. (°C)	yield (%)	molecular formula and weight	IR $V_{C=O}$ (cm^{-1})	^{1}H-NMR (CDCL$_3$) δ (ppm)	elemental analysis calcd. / found C	H	N
<u>4a</u>	H	157 - 159	25	$C_{18}H_{21}NOS_4$ 395.63	1610	1.6 (br s, 6H, 3CH$_2$) 2.1-2.4 (q, 2H, CH$_2$) 2.8-3.12 (2t, 4H, 2CH$_2$) 3.98 (br s, 4H, 2CH$_2$-N) 7.22-7.85 (m, 5H, arom.)	54.65 54.72	5.35 5.41	3.54 3.68
<u>4b</u>	Br	136 - 138	36	$C_{18}H_{20}NOS_4Br$ 474.53	1600	1.6 (br s, 6H, 3CH$_2$) 2.1-2.42 (q, 2H, CH$_2$) 2.8-3.11 (2t, 4H, 2CH$_2$-N) 3.98 (br s, 4H, 2CH$_2$-N) 7.26-7.8 (m, 4H, arom.)	45.56 44.45	4.25 4.25	2.95 2.91
<u>4c</u>	Cl	142 - 144	32	$C_{18}H_{20}NOS_4Cl$ 430.12	1610	1.62 (br s, 6H, 3CH$_2$) 2.2-2.32 (q, 2H, CH$_2$) 2.8-3.08 (2t, 4H, 2CH$_2$) 4.1 (br s, 4H, 2CH$_2$-N) 7.2-8.05 (m, 4H, arom.)	50.26 49.40	4.69 4.67	3.26 3.29
<u>4d</u>	CH$_3$	92 - 94	37	$C_{19}H_{23}NOS_4$ 409.66	1600		55.71 56.34	5.66 5.78	3.42 3.74

Results of the dithiocarboxylation of compounds with the active methylene group in neighbourhood of a sulfur atom being a component of a dithiocarbonate-type radical of the starting molecule, show that it is possible to produce either the ketene dithioacetals or the 1,3-dithiole-2-thiones in dependence on the reaction conditions.

The reaction is restricted to cases in which the thiocarbamate does not bear an acidic hydrogen at the nitrogen. The conversion of the morpholino and pyrrolidino derivatives proceeds in the considered direction, too. The reactions of 2a-d will be reported elsewhere.

Crystal and molecular structure

The final positional and thermal parameters for the atoms of 2a are listed in Table 4. Figure 1 shows the molecular structure together with the atomic numbering scheme (H atoms have the same number as the C atoms to which they are bonded, H atoms attached to the same C atom are distinguished by numbers 1 to 3). Bond lengths and angles are given in Table 5, relevant torsion angles in Table 6, and least-squares planes through various parts of the molecule in Table 7.

For a more detailed discussion of the molecular geometry in the following a formal division of the molecular skeleton into the structural fragments C_6H_5-C(O)-C=C(SCH_3)$_2$ (α-oxoketene dithioacetal fragment) and C_5H_{10}N-C(S)-S- (piperidino-dithiocarbamate fragment) seems to be useful. For a structural comparison of the former a series of related compounds investigated by X-ray analysis are known in the literature, e.g. S,S-dimethyl benzoylketene dithioacetal,[6] S,S-dimethyl (4-bromobenzoyl)-cyanoketene dithioacetal,[7] 2-(benzoyl-phenyl-methylene)-1,3-dithiolane,[8] and desaurin.[9] The observed bond lengths and angles in 2a are in good agreement with the corresponding values in the cited compounds. The C(15)-S bond lengths in 2a (1.757(3) and 1.760(3) Å) are exactly identical and equal the normal C(sp^2)-S bond length of 1.75 Å[10] whereas the C-S bond lengths to the methyl groups, at 1.793(5) and 1.804(6) Å, are also the same within the 3σ limit and only

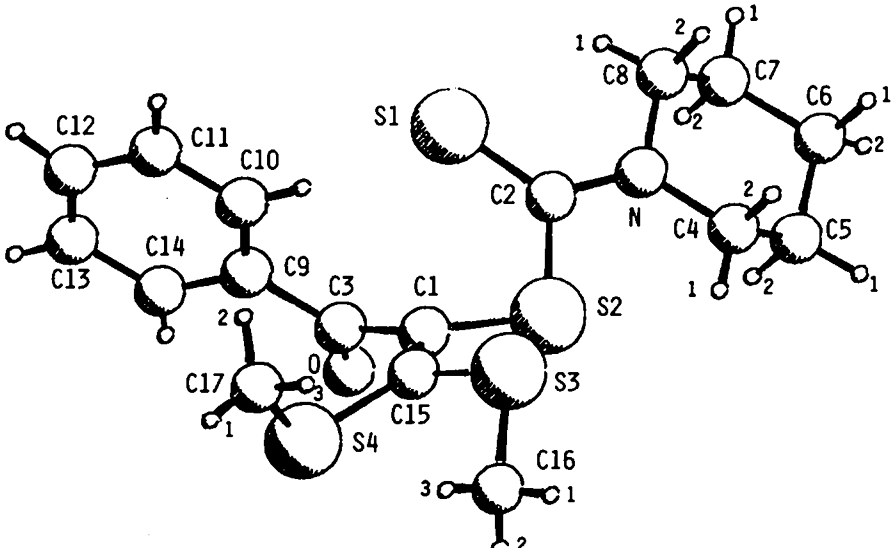


Fig. 1

Molecular structure of 2a

marginally shorter than the accepted 1.82 Å for a C(sp^3)-S bond.[10] The C(1)-C(15) bond (1.353(4) Å) is inconsiderably longer than the standard value of 1.34 Å for a C=C double bond.[10]

In contrast to the general agreement with regard to bond lengths and angles the conformation of 2a differs strongly from that observed in the above-mentioned α-oxoketene dithioacetals. The most striking structural feature reported for the latter is the close planarity of the α,β-unsaturated carbonyl and sulfur system. Associated with this planarity are S...O contact distances of about 2.7 Å which are markedly shorter than the sum of van der Waals radii of sulfur and oxygen (3.25 Å) indicating a bonding interaction. As can be clearly seen from Figure 1 and Tables 6 and

7, the $O{=}C{=}C{<}^{S}_{S}$ moiety in 2a is far from being planar. The twist of the carbonyl group out of the plane of the ethylene (best illustrated by the torsion angle O-C(3)-C(1)-C(15) = -118.7(3)°) results in loss of conjugation and is, in consequence of this, expressed by the relatively high value of the C=O frequency in the IR spectrum of 2a (Table 1). The S(4)...O distance (3.769(4) Å) is considerably longer than the normal van der Waals contact. The considerable deviations of torsion angles S(2)-C(1)-C(15)-S(3) = 22.4(2)° and S(2)-C(1)-C(15)-S(4) = -152.0(2)° from the ideal values for an exactly planar ethylene skeleton, 0° and 180°, respectively, are apparently due to the steric repulsion between the vicinal sulfur atoms. The contact distance S(2)...S(3) amounts to only 3.141(1) Å whereas the minimum van der Waals radius of sulfur observed in crystal structures is about 1.65 Å.[9] The phenyl ring is inclined by 17.7° to the l.s. plane defined by atoms C(1),C(3),C(9),O.

Atoms N,C(2),S(1),S(2),C(1) of the piperidino-dithiocarbamate fragment are closely coplanar (maximum atomic deviation 0.032(1) Å). The C(2)-N distance of 1.327(4) Å is markedly shorter than the normal C-N single bond (1.47 Å[10]). This indicates strong participation of the N lone pair in the π-system of the thiocarbonyl group and a substantial contribution of the zwitter-

Table 4. Final fractional coordinates and isotropic thermal parameters (Å^2) with estimated standard deviations in parentheses. $U_{eq} = (U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$

Atom	x/a	y/b	z/c	U_{eq}	Atom	x/a	y/b	z/c	U_{iso}
S(1)	.09395(9)	.40843(10)	.66753(7)	.0504(3)	H(41)	.321(3)	.471(4)	.387(2)	.05(1)
S(2)	.33366(9)	.60347(10)	.58038(6)	.0456(3)	H(42)	.181(4)	.442(4)	.314(3)	.08(1)
S(3)	.32574(11)	.98746(11)	.62252(7)	.0629(4)	H(51)	.341(3)	.277(4)	.235(3)	.07(1)
S(4)	.43406(9)	.98739(9)	.86487(6)	.0455(3)	H(52)	.365(4)	.200(4)	.357(3)	.10(1)
N	.1720(3)	.3493(3)	.4601(2)	.0426(9)	H(61)	.110(3)	.137(4)	.203(3)	.07(1)
O	.4371(2)	.5254(3)	.8153(2)	.0604(9)	H(62)	.211(4)	.002(4)	.218(3)	.08(1)
C(1)	.3332(2)	.7118(3)	.7183(2)	.0335(9)	H(71)	.021(3)	-.023(4)	.342(2)	.06(1)
C(2)	.1905(3)	.4395(3)	.5625(2)	.036(1)	H(72)	.165(4)	.019(4)	.415(3)	.08(1)
C(3)	.3497(3)	.6202(3)	.8154(2)	.039(1)	H(81)	.015(3)	.192(4)	.489(3)	.07(1)
C(4)	.2469(4)	.3897(4)	.3639(3)	.051(1)	H(82)	-.018(4)	.260(4)	.374(3)	.09(1)
C(5)	.2968(4)	.2392(5)	.3003(4)	.060(1)	H(100)	.108(3)	.747(4)	.833(3)	.06(1)
C(6)	.1775(4)	.0987(5)	.2625(3)	.059(1)	H(110)	-.028(4)	.787(5)	.981(3)	.10(2)
C(7)	.1008(4)	.0613(4)	.3619(3)	.057(1)	H(120)	.039(4)	.707(5)	.146(3)	.10(2)
C(8)	.0529(4)	.2129(4)	.4259(3)	.051(1)	H(130)	.253(4)	.593(5)	.169(3)	.11(2)
C(9)	.2612(3)	.6502(3)	.9117(2)	.039(1)	H(140)	.381(3)	.556(4)	.014(3)	.07(1)
C(10)	.1378(4)	.7200(4)	.9029(3)	.051(1)	H(161)	.460(5)	.203(6)	.587(4)	.14(2)
C(11)	.0568(5)	.7411(5)	.9917(4)	.069(2)	H(162)	.556(7)	.140(8)	.656(5)	.23(4)
C(12)	.0986(6)	.6944(6)	.0909(4)	.076(2)	H(163)	.445(6)	.241(6)	.705(4)	.16(2)
C(13)	.2207(7)	.6259(5)	.1016(3)	.068(2)	H(171)	.352(6)	.205(7)	.958(5)	.17(3)
C(14)	.3027(5)	.6030(4)	.0121(3)	.058(1)	H(172)	.223(6)	.089(6)	.909(5)	.17(3)
C(15)	.3564(3)	.8792(3)	.7331(2)	.037(1)	H(173)	.298(4)	.194(5)	.846(3)	.11(2)
C(16)	.4610(6)	.1637(5)	.6480(5)	.071(2)					
C(17)	.3172(7)	.1375(6)	.9042(5)	.076(2)					

Table 5. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Atoms	Distance	Atoms	Distance	Atoms	Distance
S(1)-C(2)	1.662(3)	C(1)-C(15)	1.353(4)	C(7)-C(8)	1.503(5)
S(2)-C(1)	1.763(3)	C(2)-N	1.327(4)	C(8)-N	1.482(4)
S(2)-C(2)	1.776(3)	C(3)-C(9)	1.498(4)	C(9)-C(10)	1.384(5)
S(3)-C(15)	1.757(3)	C(3)-O	1.218(4)	C(10)-C(11)	1.373(6)
S(3)-C(16)	1.793(5)	N-C(4)	1.475(5)	C(11)-C(12)	1.371(7)
S(4)-C(15)	1.760(3)	C(4)-C(5)	1.503(5)	C(12)-C(13)	1.369(8)
S(4)-C(17)	1.804(6)	C(5)-C(6)	1.509(6)	C(13)-C(14)	1.387(6)
C(1)-C(3)	1.510(4)	C(6)-C(7)	1.510(6)	C(14)-C(9)	1.385(5)

Atoms	Angle	Atoms	Angle	Atoms	Angle
C(1)-S(2)-C(2)	105.7(1)	C(9)-C(3)-O	121.0(2)	C(8)-N-C(4)	112.[illegible]

Table 5 cont'd...

S(2)-C(1)-C(3)	119.0(2)	C(1)-C(15)-S(4)	117.8(2)	C(9)-C(10)-C(11)	120.9(3)
S(2)-C(1)-C(15)	116.9(2)	C(2)-N-C(4)	125.0(2)	C(10)-C(11)-C(12)	119.9(4)
C(3)-C(1)-C(15)	121.7(2)	C(2)-N-C(8)	121.8(2)	C(11)-C(12)-C(13)	120.2(4)
S(1)-C(2)-S(2)	121.1(1)	N-C(4)-C(5)	111.3(3)	C(12)-C(13)-C(14)	120.3(4)
S(1)-C(2)-N	125.6(2)	C(4)-C(5)-C(6)	112.1(3)	C(13)-C(14)-C(9)	119.8(3)
S(2)-C(2)-N	113.4(2)	C(5)-C(6)-C(7)	109.9(3)	C(14)-C(9)-C(10)	118.9(3)
C(1)-C(3)-O	119.3(2)	C(6)-C(7)-C(8)	112.2(3)		
C(1)-C(3)-C(9)	119.8(2)	C(7)-C(8)-N	111.5(3)		

Table 6. Selected torsion angles (°)

Atoms	Angle	Atoms	Angle
N-C(2)-S(2)-C(1)	177.1(2)	C(3)-C(1)-C(15)-S(3)	-175.5(2)
S(1)-C(2)-S(2)-C(1)	-3.2(2)	C(3)-C(1)-C(15)-S(4)	10.1(2)
C(2)-S(2)-C(1)-C(3)	59.3(2)	O-C(3)-C(1)-C(15)	-118.7(3)
C(2)-S(2)-C(1)-C(15)	-138.1(2)	C(9)-C(3)-C(1)-C(15)	59.8(3)
S(2)-C(1)-C(3)-O	43.0(3)	C(1)-C(3)-C(9)-C(10)	19.0(4)
S(2)-C(1)-C(3)-C(9)	-138.5(3)	C(1)-C(3)-C(9)-C(14)	-162.4(3)
S(2)-C(1)-C(15)-S(3)	22.4(2)	O-C(3)-C(9)-C(10)	-162.5(3)
S(2)-C(1)-C(15)-S(4)	-152.0(2)	O-C(3)-C(9)-C(14)	16.1(4)

Table 7. Distances of atoms (Å) from least-squares planes with e.s.d.'s (distances enclosed in parentheses refer to atoms not included in l.s. plane calculation) and interplanar angles (°)

Atom	Plane			
	I	II	III	IV
S(1)	-0.012(1)			
S(2)	-0.032(1)	(0.722(1))	(1.028(1))	
S(3)		0.152(1)		
S(4)		0.097(1)		
N	0.021(2)			
O			-0.003(2)	
C(1)	0.025(3)	-0.127(3)	-0.002(3)	
C(2)	-0.002(3)			
C(3)	(-1.068(3))	(-0.461(3))	0.008(3)	(0.040(3))
C(9)			-0.002(3)	0.002(3)
C(10)				-0.004(4)
C(11)				0.003(4)
C(12)				-0.000(5)
C(13)				-0.002(5)
C(14)				0.001(4)
C(15)	(0.826(3))	-0.122(3)	(-1.009(3))	

Planes	Angle
I / II	119.6
I / III	84.6
I / IV	102.0
II / III	111.3
II / IV	104.5
III / IV	17.7

ionic resonance form (piperidinium structure) to the overall structure. The C(2)-S(1) distance of 1.662(3) Å is only a little but significantly shorter than the standard C=S bond length (1.70 Å^{10}). Another worth mentioning fact is the intramolecular S(1)...C(3) contact distance of 3.090(3) Å being considerably shorter than the normal S...C van der Waals contact (3.50 Å^{11}) indicating a possible dipole-dipole attractive force. This intramolecular interaction is possibly one of the factors leading to the above-described unexpected molecular conformation, although crystal packing forces may play an important role.

The observed C-H bond lengths in 2a range from 0.81(6) to 1.05(4) Å with a mean value of 0.95(6) Å. The crystal structure consists of discrete molecules with all intermolecular contacts between non-hydrogen atoms shorter than the sums of the corresponding van der Waals radii, except a closer S(4)...S(4') contact at 3.390(1) Å (symmetry code of S(4'): 1-x, 2-y, 2-z).

EXPERIMENTAL

Synthesis

The IR spectra were recorded on a 'Specord' spectrometer (VEB Carl Zeiss Jena). NMR spectra were obtained on a Varian HA 100, Bruker WP-200 and AC-80 spectrometer, respectively; chemical shifts are given in ppm values. Melting points were observed on a Boetius apparatus and are uncorrected.

General procedure for the preparation of S-(1-benzoyl-2-bis-methylthio)vinyl-piperidino-dithiocarbamates (2a-d)
To a solution of 5 mmol 1 (ref. 5) in 5 ml carbon disulfide and 5 ml chloroform is added with efficient stirring a mixture of 20 mmol potassium hydroxide and 10 mmol triethylbenzyl ammonium chloride (TEBA chloride) in 10 ml water. After 10 min at room temperature 15 mmol methyl iodide is added dropwise and stirring is continued for an hour. The phases are separated and the organic layer is washed with water and dried over anhydrous sodium sulfate. The residue obtained by evaporation of the solvent is recrystallized from ethanol or methanol.

General procedure for the preparation of α-(1,3-dithiolane-2-ylidene)-phenacyl-piperidino-dithiocarbamates (3a-d)
To a well stirred two-phase mixture of 5 mmol 1a-d, 5 ml carbon disulfide, 5 ml chloroform, 10 mmol TEBA chloride, 20 mmol KOH, and 10 ml water 7.5 mmol 1,2-dibromo-ethane is added dropwise. After an hour the organic phase is separated, washed and dried. Evaporation of the solvent gives a residue which is recrystallized from ethanol or n-butanol.

General procedure for the preparation of α-(1,3-dithiane-2-ylidene)-phenacyl-piperidino-dithiocarbamates (4a-d)
The reaction mixture is prepared according to the above described procedure. As alkylating reagent 7.5 mmol 1,3-dibromo-propane is used. Compounds 4a-d are isolated in the usual manner and purified by recrystallization from n-butanol.

General procedure for the preparation of 5-benzoyl-4-methylthio-1,3-dithiole-2-thiones (5a-d)
5 mmol 1 and 5 mmol carbon disulfide are dissolved in 50 ml dry THF. Under cooling (-10°C) and nitrogen atmosphere 10 mmol sodium hydride is added in portions. The reaction mixture is stirred for 2 h at room temperature. Then 12 mmol methyl iodide is added at once. After 2 h the solution is poured into ice. The precipitate is collected and recrystallized from n-butanol. IR and ^{1}H-NMR data are reported below.

5-Benzoyl-4-methylthio-1,3-dithiole-2-thione (5a): 49% yield, m.p. 143-145°C; IR (nujol): 1630 (C=O), 1080, 1050, 1010 (C=S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.58 (s, 3H, SCH_3), 7.9-8.3 (m, 5H, arom.)

5-(4-Bromo-benzoyl)-4-methylthio-1,3-dithiole-2-thione (5b): 27% yield, m.p. 184-186°C; IR (nujol): 1620 (C=O), 1075, 1030, 1002 (C=S) cm^{-1}. ^{1}H-NMR ($CDCl_3$/DMSO-d_6): δ 2.57 (s, 3H, SCH_3), 7.6-7.7 (m, 4H, arom.)

5-(4-Chloro-benzoyl)-4-methylthio-1,3-dithiole-2-thione (5c): 31% yield, m.p. 165-167°C; IR (nujol): 1625 (C=O), 1095, 1085, 1010 (C=S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.52 (s, 3H, SCH_3), 7.3-7.65 (m, 4H, arom.)

5-(4-Methyl-benzoyl)-4-methylthio-1,3-dithiole-2-thione (5d): 20% yield, m.p. 150-152°C; IR (nujol): 1625 (C=O), 1075, 1045, 1030 (C=S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.50 (s, 3H, SCH_3), 7.24 (d, 2H, arom.), 7.52 (d, 2H, arom.), 2.38 (s, 3H, CH_3)

Crystal structure determination

Yellow single crystals of 2a suitable for X-ray diffraction experiments were obtained by recrystallization from methanol. The relevant crystal data and experimental details are given in Table 8.

The structure was solved by direct methods using program MULTAN-80.[12] The four S atoms were found in an E map, all other non-H atoms by subsequent Fourier maps. A difference electron density map revealed the positions of all hydrogen atoms in good agreement with the theoretical positions. Full-matrix least-squares refinement with anisotropic thermal parameters for non-H atoms and isotropic ones for H atoms led to the final R = 0.036 (R_w = 0.034, counter weights, empirical extinction correction $F_{corr} = F_c(1 - 3.1\times10^{-7} F_c^2 / \sin\theta)$).

All calculations were done on an ESER 1040 computer using the programs PRARA,[13] MULTAN-80,[12] SHELX-76,[14] and EDIT.[15] Figure 1 was plotted by means of PLUTO.[16]

Table 8. Summary of crystal data and experimental details

Molecular formula and weight	$C_{17}H_{21}NOS_4$, 383.6 g mol^{-1}
Crystal system and space group	triclinic, $P\bar{1}$
Cell parameters	a = 9.586(2), b = 8.261(1), c = 12.125(2) Å
	α = 99.43(1), β = 94.14(1), γ = 97.27(1)°
	V = 935.3(3) Å^3, Z = 2, F(000) = 404
	D_c = 1.362 g cm^{-3}, D_m = 1.36(1) g cm^{-3}
Radiation	MoKα, λ = 0.71069 Å (graphite monochromator)
μ(MoKα)	4.53 cm^{-1}
Crystal size	0.28 x 0.34 x 0.37 mm
Intensity data collection	Syntex $P2_1$ diffractometer, $\theta/2\theta$ scan, bisecting mode
	$3° \leq 2\theta \leq 48°$, hkl range: -10,-9,0 to 10,9,13
Number of unique reflections	2862
Number of observed reflections	2178 with $\vert F_o \vert \geq 3.92\ \sigma(F_o)$
Final R (R_w)	0.036 (0.034)
Max. and min. heights in final $\Delta\rho$ map	0.187 and -0.197 e Å^{-3}

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