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MESOIONIC 2-N-CYCLOALKYLAMINO-5-ALKYL-1,3-DITHIOLIUM-4-THIOLATES

Magali B. De Oliveira^{ab}; Joseph Miller^{abcd}; Arnaldo B. Pereira^{bc}; Sérgio E. Galembeck^{ac}; Gustavo L. C. De Moura^e; Alfredo M. Simas^e

^a Universidade de São Paulo, Faculdade de Filosofia, Ciências e Letras, Ribeirão Preto, São Paulo, Brazil

^b Departamento de Química, Universidade Federal da Paraíba, João Pessoa, Paraíba, Brazil ^c

Universidade de São Paulo, Instituto de Química, São Paulo, São Paulo, Brazil ^d Universidade Federal da Paraíba, Laboratório de Tecnologia Farmacêutica, João Pessoa, Paraíba, Brazil ^e Departamento de Química Fundamental, Universidade Federal de Pernambuco, Recife, Pernambuco, Brazil

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MESOIONIC 2-N-CYCLOALKYLAMINO-5-ALKYL-1,3-DITHIOLIUM-4-THIOLATES

MAGALI B. DE OLIVEIRA,^{†,¶} JOSEPH MILLER,^{†,‡,§,¶}
ARNALDO B. PEREIRA,^{‡,¶} SÉRGIO E. GALEMBECK,^{†,¶}
GUSTAVO L. C. DE MOURA^{||} and ALFREDO M. SIMAS^{||}

[†]*Universidade de São Paulo, Faculdade de Filosofia, Ciências e Letras, 14040-901, Ribeirão Preto, São Paulo, Brazil;* [‡]*Universidade de São Paulo, Instituto de Química, Caixa Postal 20.780, 01498-970, São Paulo, São Paulo, Brazil;*
[§]*Universidade Federal da Paraíba, Laboratório de Tecnologia Farmacêutica, Campus I, Caixa Postal 5009, 58051-970, João Pessoa, Paraíba, Brazil;*
[¶]*Universidade Federal da Paraíba, Departamento de Química, Campus I, 58059-900, João Pessoa, Paraíba, Brazil;* ^{||}*Departamento de Química Fundamental, Universidade Federal de Pernambuco, 50670-901, Recife, Pernambuco, Brazil*

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Seven 2-(N-cycloalkylamino-1,3-dithiocarbamoyl)-carboxylic acids and seven mesoionic 2-N-cycloalkylamino-5-alkyl-1,3-dithioliium-4-thiolates have been conveniently synthesized. They were characterized by elemental analysis, I.R., U.V., mass and ¹H NMR spectrometry, plus ¹³C NMR spectrometry in some cases. Important questions concerning the structure of the mesoionic compounds, relevant to mesoionic compounds in general, are addressed. In particular, we refer to the degree of separation of regions of positive and negative charge, bond orders, electron and charge delocalization and aromaticity. In this discussion we cite some of our X-ray diffraction and theoretical studies. We conclude that there are regions of positive and negative charge in which there is delocalization of electrons and charge with bond orders between 1 and 2. However, the shared regions are separated by what are essentially single bonds. Thus, they, and mesoionic compounds in general, should not be considered as formally aromatic. This is supported by estimates of Bird Aromaticity indices—experimentally based for two of the title mesoionic compounds—of the order of 50: substantially less than values for thiophene and pyrrole and much less than values for benzene and pyridine. Finally, based on this discussion, we introduce a new notation for the structures of mesoionic compounds which we believe more accurately represents both the bonding situation and the chemical patterns of reactivity of such compounds.

Key words: Mesoionic, bond orders, charge separation, aromaticity.

1. INTRODUCTION

The study of the title compounds forms part of our on-going research on mesoionic compounds e.g., References 1–4.

Five of the seven title mesoionic compounds are new as are five of the seven intermediate dithiocarbamoyl-carboxylic acids. We present a wide range of spectroscopic and other data, while tests of biological activity, have been initiated.

Some compounds of this type were prepared by Souizi and Robert,⁵ though less conveniently.

In order to address fundamental questions of structure, electron and charge distribution and aromaticity, we cite in the present work some results of our theoretical

TABLE I

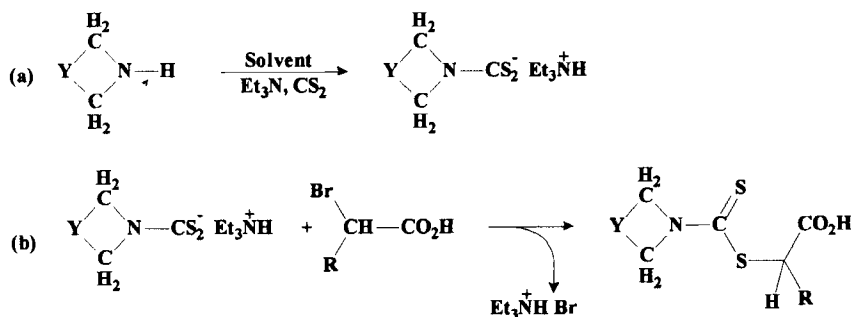
ELEMENTAL ANALYSIS		
PRODUCTS	EXPECTED	FOUND
Acid 1	C(45,60);H(6,50);N(5,31);S(24,34)	C(43,90);H(6,26);N(6,25);S(23,23)
Acid 2	Hygroscopic	
Acid 3	C(46,32);H(6,47);N(6,00);S(27,48)	C(45,19);H(6,73);N(6,13);S(25,60)
Acid 4	C(48,55);H(6,92);N(5,60);S(25,92)	C(48,17);H(6,63);N(5,39);S(23,05)
Acid 5	C(43,81);H(5,97);N(6,38);S(29,23)	C(43,78);H(5,78);N(6,06);S(29,35)
Acid 6	C(46,32);H(6,47);N(6,00);S(27,48)	C(46,16);H(6,34);N(5,57);S(25,02)
Acid 7	Hygroscopic	
P.I. 1	C(45,94);H(5,78);N(5,35);S(36,79)	C(45,40);H(5,65);N(5,67);S(36,38)
P.I. 2	C(45,94);H(5,78);N(5,35)	C(45,28);H(5,84);N(6,02)
P.I. 3	C(46,71);H(5,66);N(6,05)	C(46,73);H(5,72);N(6,75)
P.I. 4	C(48,93);H(6,16);N(5,70);S(39,19)	C(49,10);H(6,56);N(6,41);S(39,01)
P.I. 5	C(44,20);H(5,10);N(6,44);S(44,25)	C(44,32);H(5,00);N(6,11);S(43,13)
P.I. 6	C(46,71);H(5,60);N(6,05)	C(46,92);H(6,10);N(6,55)
P.I. 7	C(48,93);H(6,16);N(5,70);S(39,19)	C(49,09);H(6,27);N(6,19);S(39,29)

calculations⁶ and also our recent studies of two of the mesoionic title compounds by X-ray diffraction.⁷

EXPERIMENTAL

Preparation of 2(*N*-Cyclo-alkylamino-1,3-dithiocarbamoyl) Carboxylic Acids

Seven of these dithiocarbamoyl-carboxylic acids were prepared according to the following general scheme, discussed in the text:



where Y = CH₂CH₂; CH₂CH₂CH₂; CH₂OCH₂, R = CH₃; CH₂CH₃; CH₂CH₂CH₃; CH(CH₃)₂, solvent = light petroleum (30–60°) or toluene.

TABLE II

PRODUCTS	I.R. cm^{-1} (m)	MASS ^a	U.V. (nm)
Acid 1	3300 2500 (3.00-4.0) st. O-H ragged with max. -3000 and -2600 cm^{-1} 2900 (3.35) CH st. (CH_3 asym) 2920 (3.41) CH st. (CH_2 asym) 2860 2840 (3.5 3.51) CH st. (CH_3 sym. and CH_2 sym and or O- CH_2) 1750 1690 (5.72 5.81) st. alkyl CO and CS (broadened and rough peak) 1440 1390 (7.15 7.20) and 1320 1210 (7.6 8.35) CO st; O-H def. coupled 1200 (7.25) CH def. CH_3 asym 1270 1030 (7.8 9.0) C-S st. 1090 (8.15) C-S strong, narrow or C-O-C st. dialkyl and or C-H st. 1050 990 (9.5 10.1) S-CS H	(a) 263 (b) 163 (c) 130	281;252
Acid 2	As Acid 1 plus 1450 1400 (6.9 7.12) and 1200 1230 (7.8 8.1) CO st; O-H def. coupled 1090 1270 (7.2 7.3) def. ang. C-H (4;7.2-7.3) 1110 (9.0) C-S strong, narrow 1270 1030 (st. C-S strong, narrow or C-O-C st. 1050 (9.5) S-CS H 920 (11.0) CO OH oop		281;255
Acid 3	As Acid 1 plus 2 1450 1400 (6.9 7.2) def. C-C of piperidine ring	(a) 233 (b) 161 (c) 128	
Acid 4	As Acid 3	(a) 248 (b) 161 (c) 128	
Acid 5	As Acid 3 in the range of 1300-1100 (7.7 9.5) vibr. def. C-C alkyl. subst. of the ring	(a) 219 (b) 147 (c) 114	276;250
Acid 6	As Acid 5	(a) 234 (b) 115	
Acid 7	As Acid 5		285;240
M.I. 1 to M.I. 7	2950 (3.4) and 2915 (3.41) st. C-H (CH_3 and CH_2 asym) 2880 2850 (3.5 3.51) st. $\text{CH}(\text{CH}_3)$ and CH_2 sym) 1560 1530 (6.55-6.58) def. C-S 1480 1470 (6.8-6.81) def. ang. sym and asym. oop C-H amine 1490 1430 (6.71 7.0) vibr. def. C-C ring 1230 1200 (8.3-8.31) vibr. def. C-C alkyl 870 850 (11.5 11.7) C-S and C-S st. medium to strong	(d) 261 (e) 130 (d) 231 (e) 114	464;284 448;280 450;282 440;278 442;237 441;278

All the acids show *inter alia* (a) the molecular ion (b) aminedithiocarbamic ion radical (c) the aminothioacylium ion.

The compounds M.I. 1-6 show *inter alia* (d) the molecular ion (e) thioketene ion radical.

They were characterized by elemental analysis (Table I); I.R., U.V. and mass spectrometry (Table II); ^1H NMR (Table III) and X-ray diffraction. Physical properties and some other relevant data are given in Table IV.

The experimental details for the preparation of 2-(N-morpholino-dithiocarbamoyl)-pentanoic acid [Acid 1] follow as an example:

Preparation of 2-(N-Morpholino-1,3-dithiocarbamoyl) Pentanoic Acid (Acid 1)

Triethylamine (2.53 g; 3.5 ml; 25.1 mmole) was added at 0° with stirring to a solution of 2.0 g (2 ml; 23 mmole) of morpholine in 10 ml of light petroleum (30-60 $^\circ$). After 10 minutes, 1.70 g (1.4 ml; 23.2 mmole) of carbon disulphide was added. Triethylammonium N-morpholino-dithiocarbamate formed as a white suspension, to which was added 4.15 g (3.0 ml; 22.9 mmole) of 2-bromo-pentanoic acid dissolved in 5 ml of light petroleum. After stirring for a further 20 minutes, the reaction mixture was allowed to reach ambient temperature and stirred for a further 6 hours.

After removal of solvent by distillation, 20 ml of anhydrous benzene was added.

TABLE III

PRODUCTS	¹ H NMR (CDCl ₃) (ppm)	¹³ C NMR (CDCl ₃) (ppm)	X-ray diffraction (ref. 7)
Acid 1	1.0(t, 3H); 1.5(s, 2H); 2.0(q, 2H); 4.8(t, 1H); 3.9(methylene protons of morpholine)		
Acid 2	2.4(m, 1H); 1.1(d, 6H); 4.9(d, 1H); 4.0(methylene protons of morpholine)		
Acid 3	1.65(d, 3H); 4.8(q, 1H); 4.0(n, 4H); 1.7(n, 6H)		
Acid 4	1.05(t, 3H); 2.0(q, 2H); 4.7(t, 1H); 4.0(n, 4H); 1.7(n, 6H)		
Acid 5	1.6(d, 3H); 4.8(q, 1H); 3.95(n, 4H); 3.7(n, 4H)		
Acid 6	1.1(t, 3H); 2.1(q, 2H); 4.7(t, 1H); 4.0(n, 1H); 3.65(n, 4H)		
Acid 7	1.1(t, 3H); 2.1(q, 2H); 4.7(t, 1H); 4.0(n, 4H); 3.65(n, 4H)		
P.I. 1	1.0(t, 3H); 1.6(s, 2H); 2.7(t, 2H); 3.8(methylene protons of morpholine)		see ref 1
M.I. 2	3.8(n, 1H); 1.25(d, 6H); 3.8(methylene protons of morpholine)		
P.I. 3	2.23(s, 3H); 3.7(n, 4H); 1.8(n, 6H)		see ref 2
P.I. 4	1.20(t, 3H); 2.75(q, 2H); 3.7(n, 4H); 1.8(n, 6H)	183.4(C); 149.4(C); 128.3(C); 54.3(2C); 24.9(2C); 22.5(C); 22.0(C); 13.9(C)	
P.I. 5	2.25(s, 3H); 3.6(n, 4H); 2.25(n, 4H)		
P.I. 6	1.2(t, 3H); 2.75(q, 2H); 3.6(n, 4H); 2.25(n, 4H) (methylene protons of pyrrolidine)	178.1(C); 149.5(C); 120.4(C); 54.6(2C); 25.7(C); 22.0(2C); 13.5(C)	
P.I. 7	1.0(t, 3H); 1.6(s, 2H); 2.7(t, 2H); 3.65(n, 4H); 2.65(n, 4H); (methylene protons of pyrrolidine)	178.3(C); 150.0(C); 119.0(C); 54.7; 54.0(2C); 38.4(C); 25.7(C); 20.3(2C); 13.2(C)	

Triethylammonium bromide was removed by washing with successive portions of 5 N HCl aq. and the organic phase washed with distilled water until the washings had pH 5.

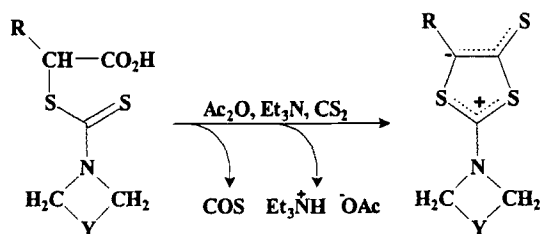
After drying the organic phase over anhydrous sodium sulphate and removal of the drying agent, the solvent was removed in a rotary evaporator at reduced pressure.

The product, 2(N-morpholino-dithiocarbamoyl) pentanoic acid was obtained in 72% yield as a clear-yellow viscous liquid, which gradually formed a waxy solid. It was characterized by elemental analysis (Table I); I.R., U.V., mass spectrometry (Table II), ¹H, ¹³C NMR spectrometry and by X-ray diffraction (Table III). Yield, m.p. and other relevant data are given in Table IV.

Acids 2 to 7 were prepared and characterized similarly (see Tables I–IV). Thus: Acid 2: 2(N-morpholino-dithiocarbamoyl-3-methyl) butanoic acid: obtained in 40% yield; Acid 3: 2(N-piperidino-dithiocarbamoyl)-propanoic acid: obtained in 95% yield; Acid 4: 2(N-piperidino-dithiocarbamoyl)-butanoic acid: obtained in 95% yield; Acid 5: 2(N-pyrrolidino-dithiocarbamoyl)-propionic acid: obtained in 86% yield; Acid 6: 2(N-pyrrolidino-dithiocarbamoyl)-butanoic acid: obtained in 83% yield; Acid 7: 2(N-pyrrolidino-dithiocarbamoyl)-pentanoic acid: obtained in 97% yield.

Preparation of Mesoionic 2-N-Cycloalkylamino-5-alkyl-1,3-dithiolium-4-thiolates

Seven title mesoionic compounds were prepared according to the following general scheme, involving three sequential reactions in a one-pot synthesis; discussed in the text:



where Y = CH₂CH₂; CH₂CH₂CH₂; CH₂OCH₂, R = CH₃; CH₂CH₃; CH₂CH₂CH₃; CH(CH₃)₂.

Note that we are using a new representation for the mesoionic ring as introduced and described in the next section.

The details of the preparation of 2-N-Morpholino-5-propyl-1,3-dithiolium-4-thiolate (MI 1) follow as an example:

2-N-Morpholino-5-propyl-1,3-dithiolium-4-thiolate (MI 1)

2-(N-Morpholino-dithiocarbamoyl)-pentanoic acid (Acid 1, 3.21 g; 12.8 mmole) was dissolved in 60 ml of anhydrous benzene at 0°. The solution was allowed to reach 10°C while adding sequentially 15.19 g (12.0 ml, 200 mmole) of carbon disulphide, 12.98 g (12.0 ml, 127 mmole) of acetic anhydride and 4.35 g (6.0 ml; 43.0 mmole) of triethylamine. The reaction mixture became yellow then carmine-red and after 15 minutes crystals began to form. It was allowed to attain ambient temperature and left overnight.

The product, obtained as a precipitate, was filtered off, washed with anhydrous benzene then recrystallized from ethanol in the form of orange needle-like crystals.

TABLE IV
Physical properties

PRODUCTS	SUBSTITUENTS		YIELD (%)	SOLVENT FOR RECRYSTALLIZATION	m.p. (°C)	MOLECULAR FORMULA	MOLECULAR WEIGHT
	R	R					
Acid 1	Morpholino	n. propyl	72	-	89.5/91.5	C ₁₀ H ₁₇ NS ₂ O ₃	263.1
Acid 2	Morpholino	isopropyl	49	-	hygroscopic	C ₁₀ H ₁₇ NS ₂ O ₃	263.1
Acid 3	Piperidino	methyl	95	-	118/124	C ₉ H ₁₅ NS ₂ O ₂	233.1
Acid 4	Piperidino	ethyl	99	-	96/104	C ₁₀ H ₁₇ NS ₂ O ₂	247.1
Acid 5	Pyrrolidino	methyl	85	-	105/108	C ₈ H ₁₃ NS ₂ O ₂	219.1
Acid 6	Pyrrolidino	ethyl	83.3	-	88.5/84.5	C ₉ H ₁₅ NS ₂ O ₂	233.1
Acid 7	Pyrrolidino	n. propyl	97.4	-	hygroscopic	C ₁₀ H ₁₇ NS ₂ O ₂	247.1
M.I. 1	Morpholino	n. propyl	75	EtOH	184/186	C ₁₀ H ₁₅ NS ₃ O	261.4
M.I. 2	Morpholino	isopropyl	72	EtOH	226.5/228.5	C ₁₀ H ₁₅ NS ₃ O	261.4
M.I. 3	Piperidino	methyl*	88	Acetone	187/189	C ₉ H ₁₃ NS ₃	231.4
M.I. 4	Piperidino	ethyl*	78.5	-	188.5/182.5	C ₁₀ H ₁₅ NS ₃	245.4
M.I. 5	Pyrrolidino	methyl	78.5	-	190/192	C ₈ H ₁₁ NS ₃	217.3
M.I. 6	Pyrrolidino	ethyl	89	EtOH	196/190	C ₉ H ₁₃ NS ₃	231.4
M.I. 7	Pyrrolidino	n. propyl	59	EtOH	175.5/177.5	C ₁₀ H ₁₅ NS ₃	245.4

* - Already reported in the literature (ref. 5)

It was characterized by elemental analysis (Table I); I.R., U.V. and mass spectrometry (Table II), ^1H NMR and X-ray diffraction (Table III). Yield, M.P. and other relevant data are given in Table IV.

Six more title mesoionic compounds MI 2 to MI 7 were similarly prepared and characterized. For MI 4, MI 6 and MI 7 some ^{13}C NMR data are included in Table III. MI 2: 2-N-Morpholino-5-isopropyl-1,3-dithiolium-4-thiolate: obtained in 72% yield; MI 3: 2-N-Piperidino-5-methyl-1,3-dithiolium-4-thiolate: obtained in 80% yield; MI 4: 2-N-Piperidino-5-ethyl-1,3-dithiolium-4-thiolate: obtained in 72% yield; MI 5: 2-N-Pyrrolidino-5-methyl-1,3-dithiolium-4-thiolate: obtained in 79% yield; MI 6: 2-N-Pyrrolidino-5-ethyl-1,3-dithiolium-4-thiolate: obtained in 89% yield; MI 7: 2-N-Pyrrolidino-5-propyl-1,3-dithiolium-4-thiolate: obtained in 59% yield. See Tables I–IV.

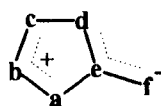
2. RESULTS AND DISCUSSION

Key questions as regards the structure of the title compounds and, indeed, of mesoionic compounds in general relate to (a) the degree of separation of positive and negative charge (b) bond-orders, in particular those of the bonds which separate the regions of positive and negative charges (c) electron delocalization and aromaticity. The results of some of our theoretical studies⁶ and of our X-ray diffraction studies⁷ are particularly relevant and are summarized in Table V.

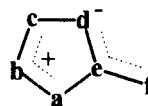
We have published two definitions of mesoionic compounds.^{8,9} Our current definition, based on our theoretical studies (semi-empirical MNDO/PM3¹⁰ and AM1¹⁰) and chemical evidence, is as follows:

Mesoionic compounds are planar five-membered heterocyclic betaines with at least one side chain whose α -atom is also in the ring plane and with dipole moments of the order of 5D. Electrons are delocalized over two regions separated by what are essentially single bonds. One region, which includes the α -atom of the side-chain, is associated with the HOMO and negative π charge whereas the other is associated with the LUMO and positive π charge.

Hence, we now conveniently introduce representative structures (I) and (II) for type A mesoionic compounds, which constitute an overwhelming majority of these unusual heterocycles¹¹ and which are coherent with our new definition.



(I)



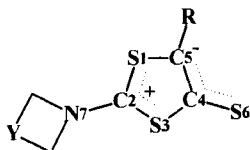
(II)

The basic chemical structure of the title compounds (omitting details of the struc-

TABLE V
Summary of results of MNDO-PM3 calculations and comparison with X-ray diffraction data for 2-N-morpholino-5-propyl-1,3-dithiolium-4-thiolate

Bonds	Bond Orders	Distances (Å)	X-Ray diffraction distances (Å)
S3-C2	1.11	1.724	1.710
C2-S1	1.17	1.736	1.715
S1-C5	1.03	1.738	1.764
C5-C4	1.53	1.374	1.346
C4-S6	1.40	1.610	1.719
C2-N7	1.37	1.366	1.321
S3-C4	0.89	1.808	1.753

ture of the saturated heterocyclic rings attached by nitrogen at the 2-position in the mesoionic ring) corresponds to (II) and this is because the HOMO squared, which is its contribution to the electron density, is concentrated on C5 while the LUMO squared is concentrated on C2. This is coherent with the behavior of this mesoionic system as a 1-3-dipole in which the π negative charge is concentrated on C5 and the π positive charge is concentrated on C2.



It should be stressed that the concept of well-separated positive and negative charge in mesoionic compounds is widely accepted. Obvious support comes from the large values of dipole moment which have been reported: an early reference¹² is that of Lefèvre *et al.*, in which dipole moments of about 7D were reported for several sydnone (1,2,3-oxadiazolium-5-olates).

Interestingly, our own kinetic study¹³ of some mesoionic compounds led to the same general conclusion. In that study of aromatic nucleophilic substitution reactions of 1,3-diphenyl-2-[4-chloro-3-nitrophenyl]-1,3,4-triazolium-5-thiolate with some anionic and neutral nucleophiles, it could be inferred that the regions of positive and negative charge in that mesoionic system are so well-separated that the substrate, though neutral overall, *behaves as a pair of ions with respect to solvation*.

These various comments suggest that the title compounds should not be classed as formally aromatic despite the substantial level of electron delocalization.

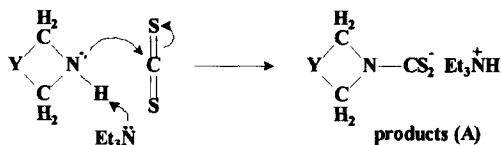
This is further clarified by the use of Bird aromaticity indices.^{14,15} From the structures of 2-N-piperidino-5-methyl-1,3-dithiolium-4-thiolate and 2-N-morpholino-5-propyl-1,3-dithiolium-4-thiolate determined by our X-ray diffraction studies⁷ we estimated their Bird aromaticity indices as 53 and 50 respectively. This compares with values of 51 and 50 which we calculated⁹ by the MNDO-PM3 method; while for the model compound 2-amino-1,3-dithiolium-4-thiolate we calculated the index as equal to 49.

Bird^{14a} has, interestingly, cited aromaticity indices for 19 mesoionic systems, though none are similar to the title compounds. Of these, 11 have larger aromaticity indices, 5 have smaller indices and 3 have aromaticity indices in the same range as the title compounds.

These values may be compared with Bird aromaticity indices for some standard compounds taken from a more recent compilation,¹⁵ viz., benzene 100, pyridine 86, pyrrole 69, thiophene 66, furan 43.

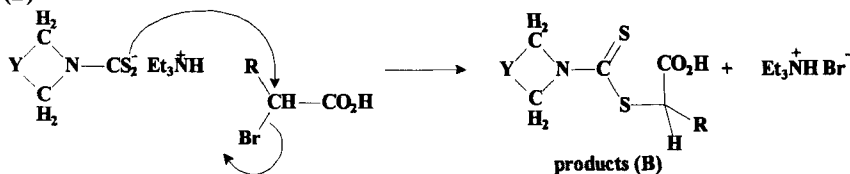
The synthesis of the title compounds described in the experimental section involves a varied sequence of reaction types, viz., (A) nucleophilic addition to heteropolar unsaturated carbon; (B) nucleophilic substitution at saturated carbon; (C) cyclo-dehydration; (D) 1,3-dipolar addition; (E) retro-1,3-dipolar addition. Details follow:

(A)



Formation of triethylammonium 2-N-cycloalkylamino-dithiocarbamates by nucleophilic addition of three different saturated heterocyclic secondary amines to carbon disulfide in the presence of triethylamine.

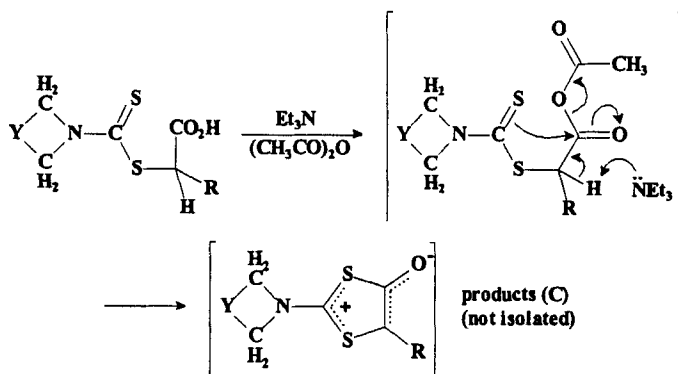
(B)



Formation of 2-N-cycloalkylamino-dithiocarbamoyl-carboxylic acids by reactions of the products of reactions (A), as nucleophiles, with four different α -bromo-carboxylic acids.

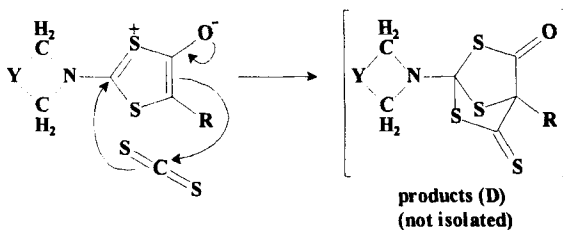
Reactions (C), (D) and (E) occur as a one-pot reaction in which the reaction products (B) then react with acetic anhydride and carbon disulfide in the presence of triethylamine. Thus:

(C)

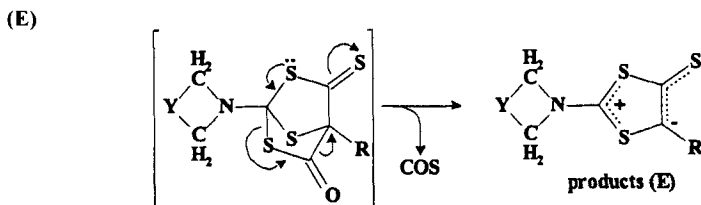


Formation of 2-N-cycloalkylamino-5-alkyl-1,3-dithiolium-4-olates in a cyclo-dehydration reaction via the mixed anhydride formed *in situ*.

(D)



Formation of adducts by 1,3-dipolar addition of products (C) to carbon disulfide.



Formation of the title mesoionic compounds by retro-1,3-dipolar addition, eliminating carbon oxysulfide from the adducts (D).

In carrying out reactions (A) and (B), we prepared and isolated, in yields generally in excess of 80%, seven 2-N-cycloalkylamino-dithiocarbamoyl-carboxylic acids: Ac 1 to Ac 7, viz., Ac 1: 2-N-morpholino-dithiocarbamoyl-pentanoic acid; Ac 2: 2-N-morpholino-dithiocarbamoyl-3-methyl-butanoic acid; Ac 3: 2-N-piperidino-dithiocarbamoyl-propanoic acid; Ac 4: 2-N-piperidino-dithiocarbamoyl-butanoic acid; Ac 5: 2-N-pyrrolidino-dithiocarbamoyl-propanoic acid; Ac 6: 2-N-pyrrolidino-dithiocarbamoyl-butanoic acid; Ac 7: 2-N-pyrrolidino-dithiocarbamoyl-pentanoic acid.

Five of these are new, while all the compounds were characterized by elemental analysis, m.p. (except Ac 2 and Ac 7); I.R. and U.V. spectroscopy; and by ^1H NMR spectrometry.

By the one-pot sequence of reactions (C)(D)(E), the compounds Ac 1 to Ac 7 were converted to seven 2-N-cycloalkylamino-5-alkyl-1,3-dithiolium-4-thiolates, MI 1 to MI 7. MI 1: 2-N-morpholino-5-propyl-1,3-dithiolium-4-thiolate; MI 2: 2-N-morpholino-5-isopropyl-1,3-dithiolium-4-thiolate; MI 3: 2-N-piperidino-5-methyl-1,3-dithiolium-4-thiolate; MI 4: 2-N-piperidino-5-ethyl-1,3-dithiolium-4-thiolate; MI 5: 2-N-pyrrolidino-5-methyl-1,3-dithiolium-4-thiolate; MI 6: 2-N-pyrrolidino-5-ethyl-1,3-dithiolium-4-thiolate; MI 7: 2-N-pyrrolidino-5-propyl-1,3-dithiolium-4-thiolate.

Five of these are new, while all the compounds were characterized by elemental analysis; m.p., I.R., U.V., mass and ^1H NMR spectrometry; some also by ^{13}C NMR spectrometry.

Some other derivatives of this class were prepared by Souizi and Robert⁵ via dithiocarbamoyl-carboxylic acids.

These however, were prepared in a less convenient way than in the present work, using less accessible and less convenient precursors.

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