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SYNTHESIS OF SOME 4,5,6,7-TETRATHIOCINO [1,2-b:3,4-b'] DIIMIDAZOLYL-1,3,8,10-TETRASUBSTITUTED-2,9-DITHIONES AND CRYSTAL STRUCTURE OF THE TETRAETHYL DERIVATIVE

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SYNTHESIS OF SOME 4,5,6,7-TETRATHIOCINO [1,2-b:3,4-b'] DIIMIDAZOLYL-1,3,8,10- TETRASUBSTITUTED-2,9-DITHIONES AND CRYSTAL STRUCTURE OF THE TETRAETHYL DERIVATIVE

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A new unexpected molecule has been obtained by reacting 1,3-disubstituted-imidazolidinetrione-2-thio derivatives (R = Methyl, Ethyl, Phenyl, *o*-Tolyl) with Lawesson's reagent. The X-ray structure of a crystal of this material (R = Ethyl) demonstrated that the title compound with an eight-membered ring composed of four S and four C-atoms was formed. The crystals are monoclinic, space group $C2/c$, $a = 18.071(4)$, $b = 9.447(2)$, $c = 14.952(3)\text{\AA}$, $\beta = 126.14(2)^\circ$, $V = 2061.4(9)\text{\AA}^3$, $Z = 4$. Solution and refinement of intensity data gave final residuals of $R = 0.0354$ and $R_w = 0.0426$ using 1090 observed reflections [$I \geq 2\sigma(I)$]. In the molecule the eight membered ring adopts a chair conformation; in the $-\text{C}-\text{C}-\text{C}-\text{C}-$ moiety the $\text{C}(3)-\text{C}(3')$ bond length is shorter than that of a single bond and the imidazolidine rings are not planar.

INTRODUCTION

We are studying charge-transfer complexes of I_2 with molecules containing $\text{NC}=\text{X}$ ($\text{X} = \text{S}$ or Se) groups, both free and coordinated to transition metals. These c.t. complexes may either be inert compounds^{1,2,3} or intermediates in redox reaction.^{4,5,6}

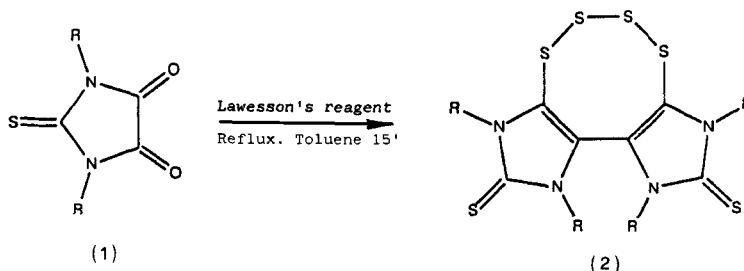
While there is no reason to predict different reactivities of similar molecules with the same functional groups, we have often observed different reaction courses. For example, the dithiomalonamide. I_2 complexes evolve with a fast reaction (results to be published) to give the known dithiolium iodide,⁷ while the dithiooxamide. I_2 counterparts are inert complexes in the 1:1 and 1:2 stoichiometries.⁸ X-ray results show that the torsion angle $\text{S}-\text{C}-\text{C}-\text{S}$ is $\sim 90^\circ$, and that there is extensive delocalization within $\text{NC}(\text{S})$ moieties but not along the carbon-carbon skeleton between them in the dithiooxamide bis(diiodine) molecule.

In an attempt to synthesize a molecule with two adjacent $\text{C}=\text{S}$ groups forced in cis position, in order to study the effect of geometrical changes on the course of the reaction, we reacted 1,3-disubstituted imidazolidinetrione-2-thio derivatives

with Lawesson's reagent and we obtained surprisingly the corresponding title compounds.

RESULTS AND DISCUSSION

The reaction of 1,3-disubstituted imidazolidinetrione-2-thio derivatives obtained by literature methods,⁹ with Lawesson's reagent¹⁰ in refluxing toluene, gave the corresponding 4,5,6,7-tetrathiocino[1,2-b:3,4-b']diimidazolyl-1,3,8,10-tetrasubstituted-2,9-dithiones, according to the reaction scheme reported below.



These new derivatives have been analytically and spectroscopically characterized, as described in experimental part. X-ray results have revealed that the molecular structure of (2) ($R = \text{Ethyl}$) is as shown in Figure 1.

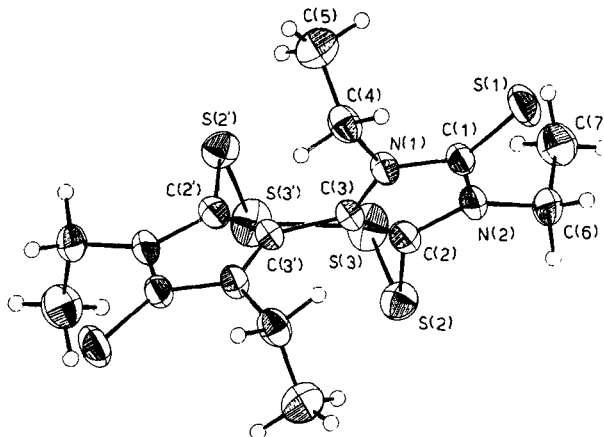


FIGURE 1 Perspective view of the molecule. Thermal ellipsoids are drawn at the 40% probability level. The primed atoms are related to the unprimed ones by a crystallographic two-fold axis.

Fractional atomic coordinates are presented in Table I; bond distances and angles are listed in Table II.

In the molecule the two

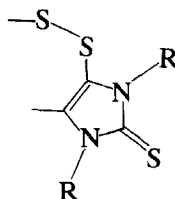


TABLE I

Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses:

	X/a	Y/b	Z/c		X/a	Y/b	Z/c
S1	3255(1)	1812(1)	-1061(1)	C7	2701(3)	5636(5)	-1199(3)
S2	3653(1)	5692(1)	1907(1)	H1	5436(37)	920(58)	2112(49)
S3	4355(1)	7326(1)	1779(1)	H2	4764(35)	486(58)	824(43)
N1	4464(2)	2356(3)	1152(2)	H3	6203(47)	1238(74)	1375(55)
N2	3327(2)	3849(3)	272(2)	H4	6155(49)	2670(84)	1634(59)
C1	3682(2)	2681(4)	126(3)	H5	5452(48)	2222(76)	396(64)
C2	3898(2)	4282(4)	1382(3)	H6	2100(38)	3809(59)	-1178(48)
C3	4607(2)	3357(3)	1922(2)	H7	2173(36)	5067(61)	-351(44)
C4	5120(3)	1274(4)	1339(3)	H8	3057(43)	5076(78)	-1447(52)
C5	5795(3)	1838(5)	1157(4)	H9	2190(56)	6114(80)	-1755(66)
C6	2493(2)	4567(4)	-633(3)	H10	3139(52)	6254(80)	-704(65)

TABLE II

Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

S2—S3	2.077(2)	C4—C5	1.496(9)
S3—S3'	2.038(2)	C6—C7	1.501(7)
S1—C1	1.675(4)	C4—H1	1.00(6)
S2—C2	1.731(5)	C4—H2	0.99(5)
N1—C1	1.374(4)	C5—H3	0.83(7)
N1—C3	1.391(4)	C5—H4	1.00(7)
N1—C4	1.462(6)	C5—H5	0.99(8)
N2—C1	1.357(5)	C6—H6	1.00(5)
N2—C2	1.402(4)	C6—H7	1.01(8)
N2—C6	1.469(4)	C7—H8	1.05(9)
C2—C3	1.355(4)	C7—H9	0.92(7)
C3—C3'	1.452(3)	C7—H10	0.91(7)
S1—C1—N1	127.0(3)	C5—C4—H1	111(4)
S1—C1—N2	127.1(3)	C5—C4—H2	111(4)
N1—C1—N2	105.9(3)	H1—C4—H2	108(5)
C1—N1—C3	109.8(3)	C4—C5—H3	108(5)
C1—N1—C4	123.6(3)	C4—C5—H4	114(5)
C3—N1—C4	125.7(3)	C4—C5—H5	108(5)
N1—C3—C2	107.2(3)	H3—C5—H4	102(7)
N1—C3—C3'	124.0(3)	H3—C5—H5	121(7)
C2—C3—C3'	128.8(3)	H4—C5—H5	104(6)
C3—C2—N2	107.1(3)	N2—C6—H6	106(3)
S2—C2—N2	123.7(3)	N2—C6—H7	111(3)
S2—C2—C3	129.1(3)	C7—C6—H6	108(3)
C1—N2—C2	109.9(3)	C7—C6—H7	108(3)
C1—N2—C6	123.6(3)	H6—C6—H7	112(6)
C2—N2—C6	126.5(3)	C6—C7—H8	106(4)
N1—C4—C5	111.9(3)	C6—C7—H9	113(7)
N2—C6—C7	111.6(4)	C6—C7—H10	111(5)
C2—S2—S3	101.3(2)	H8—C7—H9	115(6)
S2—S3—S3'	106.4(1)	H8—C7—H10	101(8)
N1—C4—H1	108(4)	H9—C7—H10	110(7)
N1—C4—H2	107(4)		

Key to symmetry operations ('): 1 - x, y, 1/2 - z

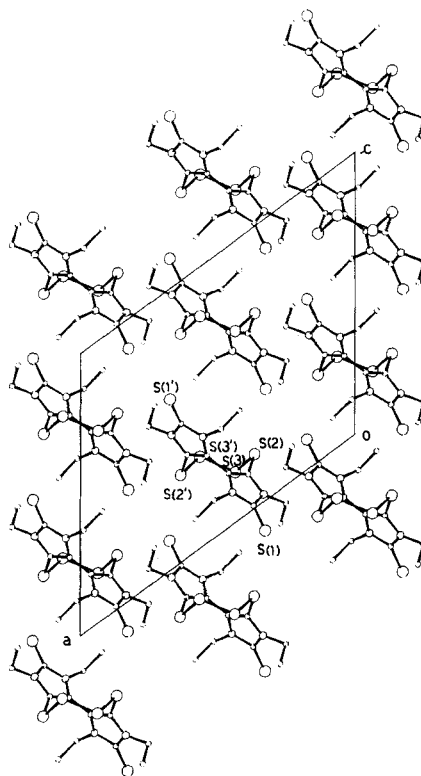


FIGURE 2 Projection of the structure viewed along *b*.

moieties are related by a crystallographic two-fold axis. The imidazoline ring is not exactly planar (maximum deviation $0.013(4)\text{\AA}$ for C(1)). The two ethyl substituents lie quite perpendicular to the ring [$C(1)-N(1)-C(4)-C(5)$ 84° , $C(1)-N(2)-C(6)-C(7)$ -87°] to yield the minimum hindrance and are responsible for the orientation of the two imidazoline rings in the molecule [$N(1)-C(3)-C(3')-N(1')$ -70°]. The eight-membered ring adopts a chair-conformation, as indicated by the torsion angles [$S(2)-S(3)-S(3')-S(2')$ 78° , $C(2)-C(3)-C(3')-C(2')$ -68° , $C(2)-S(2)-S(3)-S(3')$ -89° , $S(3)-S(2)-C(2)-C(3)$ 90°]. In the $-C-C-C-C-$ moiety the $C(3)-C(3')$ bond length [$1.452(3)\text{\AA}$] between the two double bonds involved in the fusion with the imidazoline rings, is clearly shorter than that of a single-bond. The $S(2)-S(3)$ bond distance [$2.077(2)\text{\AA}$] is related to the values of the $S(3)-S(2)-C(2)-C(3)$ torsion angle, as observed in uncomplexed disulphides.

The packing is determined by Van der Waals contacts of type $S \cdots C_{\text{aliph}}$ (see Figure 2).

CONCLUSIONS

In this paper we have described the unexpected formation of a series of a large ring tetrasulphur compounds, while no expected sulphur counterparts have been

observed by means of the thiation reaction of the 1-3 dialkylimidazolidinetrione-2-thio. A mechanistic study to investigate these reactions, may also help to understand why α -dithiones containing a five or six-membered ring are uncommon.¹¹

Moreover the uniqueness of the structure of these compounds shows interesting coordinating properties now under investigation.

In fact this molecule shows coordinative properties towards I_2 and transition metals.

A 1:2 charge-transfer adduct with diiodine (R = Ethyl) has been already prepared and X-ray results indicate that of the several electron-donor sites available in the molecule the two S atoms of the thioketonic groups are responsible for the donation (C(1)—S(1) distance = 1.689(5) Å; S(1)— I_2 distance = 2.765(5) Å). No higher stoichiometries have been evidenced.

Also this molecule can behave as bidentate-bridging ligand towards transition metals as Pd(II), Cd(II), Hg(II) ecc. A complex with Cu(II), having formula $[CuCl_2L]_n$ has been isolated (R -Ethyl), and X-ray structure shows a polymeric chain in which the Cu atom is coordinated by two chlorine atoms and two thioketonic sulphur atoms of different ligand molecules. A study on the magnetic properties of these polymers is in progress.

EXPERIMENTAL

I.R. spectra were recorded on a Perkin Elmer mod 983 spectrophotometer as KBr pellets; U.V. spectra were recorded in $CHCl_3$ on a Cary 2300 instrument and CHN analyses were performed by Istituto di Chimica Farmaceutica, University of Cagliari.

The 1,3-disubstituted imidazolidinetrione-2-thio derivatives (1) (R = Methyl, Ethyl, Phenyl, *o*-Tolyl) were prepared by literature methods.⁹ They were refluxed 15' in toluene with a slight excess of Lawesson's reagent¹⁰ and the solvent was rotary evaporated. The crude residue was extracted with dichloromethane and by addition of ethanol the title compounds (2) were obtained as well formed air-stable yellow crystals, in nearly quantitative yield.

4,5,6,7-Tetrathiocino[1,2-b: 3,4-b']diimidazolyl-1,3,8,10-tetramethyl-2, 9-dithione. IR (cm^{-1} ; KBr pellets): 2975 vw, 2931 vw, 1468 m, 1431 s, 1401 s, 1378 vs, 1362 vs, 1322 s, 1292 m, 1162 s, 1100 mw, 1078 mw, 1030 m, 861 mw, 839 mw, 731 w, 698 w, 615 w, 559 w, 539 m, 445 w, 421 m, 375 m; UV(nm, (log ϵ)): 325, (4.35); 270, (4.84).

Found: C37.56; H4.25; N18.27. Calc. for $C_{10}H_{12}N_4S_6$: C37.97; H3.82; N17.71

4,5,6,7-tetrathiocino [1,2-b: 3,4-b'] diimidazolyl-1,3,8,10-tetraethyl-2, 9-dithione. IR (cm^{-1} ; KBr pellets): 2985 m, 2940 m, 2870 w, 1435 ms, 1401 vs, 1370 s, 1332 ms, 1307 m, 1268 vs, 1156 s, 1091 m, 1050 w, 980 w, 958 w, 821 w, 810 m, 778 w, 690 w, 610 w, 549 w, 420 w, 392 w, 358 w, UV(nm, (log ϵ)): 334, (4.01); 274, (4.56).

Found: C38.06; H4.34; N12.19. Calc. for $C_{14}H_{20}N_4S_6$: C38.50; H4.62; N12.83

4,5,6,7-tetrathiocino [1,2-b: 3,4-b']diimidazolyl-1,3,8,10-tetraphenyl-2, 9-dithione. IR(cm^{-1} , KBr pellets): 3100 sh, 3059 w, 3039 w, 3016 sh, 1591 m, 1491 s, 1450 mw, 1384 sh, 1365 vs, 1351 vs, 1327 vs, 1300 vs, 1285 sh, 1170 w, 1155 w, 1070 m, 1021 w, 1004 w, 980 w, 775 m, 750 s, 696 s, 678 s, 624 m, 610 w, 517 m, 415 wbr. UV(nm, (log ϵ)): 292(4.37); 330 sh.

Found: C54.78; H3.12; N7.96. Calc. for $C_{30}H_{20}N_4S_6$: C57.30; H3.21; N8.91

4,5,6,7-tetrathiocino[1,2-b: 3,4-b'] diimidazolyl-1,3,8,10-tetra-*o*-tolyl-2,9-dithione. IR(cm^{-1} ; KBr pellets): 3054 mw, 3027 mw, 2972 mw, 2917 mw, 2853 mw, 1602 w, 1579 w, 1487 vs, 1456 s, 1363 vs, 1346 vs, 1322 vsbr, 1203 m, 1157 m, 1120 m, 1039 m, 978 m, 944 vw, 861 vw, 775 sh, 762 s, 740 s, 729 s, 712 m, 688 vw, 626 s, 563 vw, 536 w, 488 w, 451 m, 407 m. UV(nm, (log ϵ)): 335, (4.00); 286 (4.48)

Found: C54.95; H3.79; N7.05. Calc. for $C_{34}H_{28}N_4S_6CH_2Cl_2$: C 54.60; H 3.93; N7.28.

Structure determination. The cell parameters were determined by least-squares refinement from the values of 30 reflections accurately measured on a Siemens AED diffractometer using Cu—K α radiation. The intensity data were collected in the $\theta - 2\theta$, mode (with θ in the range 3–70°). The space group was to be C2/c. Of 1964 independent reflections measured, 1090 were considered as observed [$I \geq 2\sigma(I)$]. Only Lorentz-polarization corrections were applied. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares,¹² with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were located from a ΔF map and their coordinates were introduced in the last cycle. Convergence was reached at $R = 0.0354$.

Crystal data. C₁₄H₂₀N₄S₆, $M = 436.698$. Monoclinic space group C2/c, $a = 18.071(4)$, $b = 9.447(2)$, $c = 14.952(3)$ Å, $\beta = 126.14(2)^\circ$, $V = 2061.4(9)$ Å³, $Z = 4$, $\mu[\text{Cu-K}\alpha] = 60.96 \text{ cm}^{-1}$, $F(000) = 912$, $\lambda = 1.541838$ Å.

Note. The tables of anisotropic or isotropic thermal parameters and of the experimental data for the crystallographic analysis of (2) are deposited with the Cambridge Crystallographic Data Center (CCDC) U.K.

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