REACTIONS OF POLYHALOPYRIDINES.

1. REACTION OF THE ISOMERIC TETRACHLOROCYANOPYRIDINES AND PENTACHLOROPYRIDINE WITH SALTS OF N,N-DIALKYLDITHIOCARBAMIC ACID AND THE X-RAY STRUCTURAL INVESTIGATION OF THE REACTION PRODUCTS

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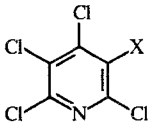
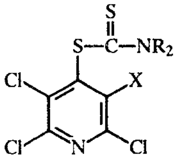
The route of the reaction of the isomeric tetrachloro-2-, -3-, -4-cyanopyridines and of pentachloropyridine with sodium N,N-dialkyldithiocarbamates is determined by the structure of the initial polyhalopyridine. Either substitution of chlorine atoms on the pyridine ring by a dithiocarbamate fragment occurs or subsequent intramolecular processes take place leading to a derivative of 1,3-dithiolo[4,5-c]pyridine or of bis-1,3-dithiolo[4,5-b:4'5'-e]pyridine.

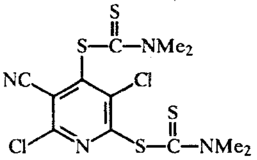
Polychloropyridines are compounds reactive in nucleophilic substitution reactions and are widely used as intermediates in the synthesis of a whole range of agrochemical preparations [1]. Nucleophilic mono- and disubstitution at positions 2 and 4 of the pyridine ring are the most characteristic [2]. Highly reactive reagents [3] or the action of high temperature [4] is required for polysubstitution but reaction may also be accelerated significantly by intramolecular processes [5].

In this paper we report a new method of synthesizing the 1,3-dithiolo[4,5-c]pyridine and bis-1,3-dithiolo[4,5-b:4',5'-e]pyridine systems based on the intramolecular reaction of N,N-dialkyldithiocarbamates of polychloropyridines. Compounds containing these systems possess high biological activity [6].

The reaction of pentachloropyridine (Ia) and of the isomeric tetrachloro-3-, -4-, and -2-cyanopyridines (Ib-d) with sodium N,N-dialkyldithiocarbamates in acetone has been studied under various temperature regimens. It has been shown that in the first case a regioselective nucleophilic monosubstitution occurs at position 4 of the pyridine ring (IIa, c) but the formation of two substances, viz., the products of mono- (IIb) and disubstitution (III), is characteristic of compound (Ic). Compounds (IIa-c) and (III) are stable and are not subject to further conversion on heating (boiling in various solvents).


Ia,b


II


III

I, IIa X = Cl, R = Me; b X = CN, R = Me; c X = Cl, R = CH_2Ph

On reacting sodium dimethyldithiocarbamate with tetrachloro-4-cyanopyridine (Ic) a 2,6-disubstitution occurs with the formation of compound (IV), which on heating is converted in turn into the intermediate (V) and then into compound (VI). Sequential conversions of compound (IV) into (V), and of (V) into (VI) support the scheme given below (see following page).

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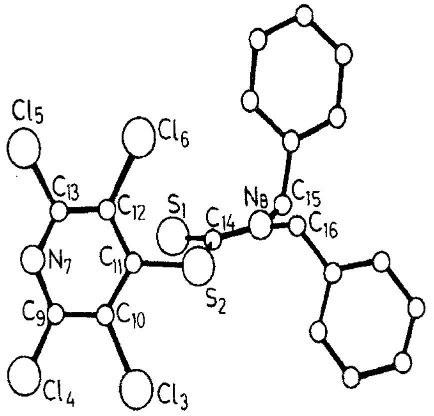


Fig. 1 Structure of 2,3,5,6-tetrachloro-4-pyridyl N,N-dibenzyldithiocarbamate (IIc).

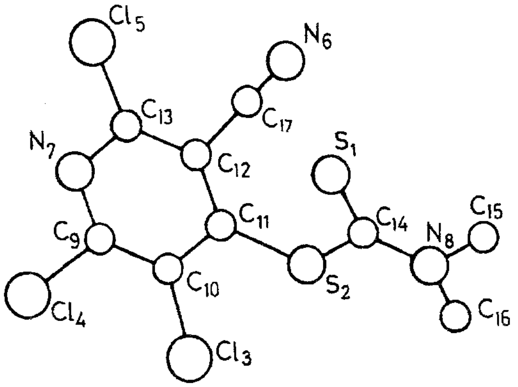
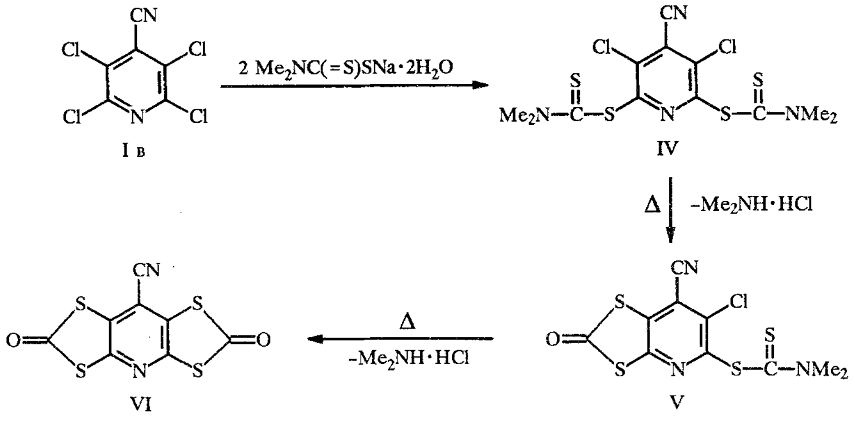


Fig. 2. Structure of 2,3,6-trichloro-5-cyano-4-pyridyl N,N-dimethyldithiocarbamate (IIb).



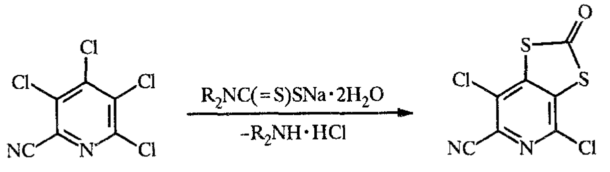
Unlike the previous cases compound (Id) is readily converted by hydrates of sodium dialkyldithiocarbamates into 4,7 dichloro-6-cyano-1,3-dithiolo[4,5-c]pyrid-2-one (VII). The composition of the amine portion of the dithiocarbamate does not exert a significant effect on the yield of (VII) or on the reaction conditions (see scheme on following page).

The structures of the compounds synthesized were confirmed by a set of physicochemical methods including x-ray structural analysis and NMR. The structures of the (IIc) and (IIb) molecules are shown in Figs. 1 and 2 respectively. Bond lengths and valence angles are given in the single Table 1 for convenience in making comparisons.

TABLE 1. Bond Lengths (d) and Valence Angles (ω) in Compounds (IIb) and (IIc)

Bond	d, Å(IIc)	d, Å(IIb)	Bond	d, Å(IIc)	d, Å(IIb)
$S_{(1)}$—$C_{(14)}$	1,670(5)	1,648(5)	$N_{(8)}$—$C_{(15)}$	1,467(7)	1,494(9)
$S_{(2)}$—$C_{(11)}$	1,764(5)	1,761(6)	$N_{(8)}$—$C_{(16)}$	1,478(6)	1,467(8)
$S_{(2)}$—$C_{(14)}$	1,789(6)	1,787(5)	$C_{(9)}$—$C_{(10)}$	1,379(8)	1,368(7)
$Cl_{(3)}$—$C_{(10)}$	1,838(7)	1,713(6)	$C_{(10)}$—$C_{(11)}$	1,372(7)	1,389(7)
$Cl_{(4)}$—$C_{(9)}$	1,681(5)	1,708(6)	$C_{(11)}$—$C_{(12)}$	1,390(9)	1,409(8)
$Cl_{(5)}$—$C_{(13)}$	1,733(5)	1,735(5)	$C_{(12)}$—$C_{(13)}$	1,345(7)	1,367(7)
$N_{(7)}$—$C_{(9)}$	1,355(7)	1,348(7)	$N_{(6)}$—$C_{(17)}$		1,134(8)
$N_{(7)}$—$C_{(13)}$	1,331(6)	1,315(6)	$Cl_{(6)}$—$C_{(12)}$	1,882(6)	
$N_{(8)}$—$C_{(14)}$	1,321(7)	1,321(7)			

Angle	ω(IIc)	ω(IIb)	Angle	ω(IIc)	ω(IIb)
$C_{(11)}$—$S_{(2)}$—$C_{(14)}$	100,9(2)	101,7(3)	$C_{(10)}$—$C_{(11)}$—$C_{(12)}$	116,8(5)	117,5(5)
$C_{(9)}$—$N_{(7)}$—$C_{(13)}$	117,3(4)	117,2(5)	$C_{(11)}$—$C_{(12)}$—$C_{(13)}$	119,2(5)	118,6(5)
$C_{(14)}$—$N_{(8)}$—$C_{(15)}$	122,3(5)	118,9(5)	$Cl_{(5)}$—$C_{(13)}$—$N_{(7)}$	113,8(3)	115,6(4)
$C_{(14)}$—$N_{(8)}$—$C_{(16)}$	124,0(4)	124,1(5)	$Cl_{(5)}$—$C_{(13)}$—$C_{(12)}$	121,4(4)	120,1(4)
$C_{(15)}$—$N_{(8)}$—$C_{(16)}$	113,6(4)	116,8(5)	$N_{(7)}$—$C_{(13)}$—$C_{(12)}$	124,6(5)	124,2(5)
$Cl_{(4)}$—$C_{(9)}$—$N_{(7)}$	117,1(4)	114,1(4)	$S_{(1)}$—$C_{(14)}$—$S_{(2)}$	121,1(3)	121,3(3)
$Cl_{(4)}$—$C_{(9)}$—$C_{(10)}$	122,4(4)	122,3(4)	$S_{(1)}$—$C_{(14)}$—$N_{(8)}$	125,3(4)	126,3(4)
$N_{(7)}$—$C_{(9)}$—$C_{(10)}$	120,5(5)	123,5(5)	$S_{(2)}$—$C_{(14)}$—$N_{(8)}$	113,6(4)	112,4(4)
$Cl_{(3)}$—$C_{(10)}$—$C_{(9)}$	116,8(4)	120,0(4)	$N_{(6)}$—$C_{(17)}$—$C_{(12)}$		176,3(7)
$Cl_{(3)}$—$C_{(10)}$—$C_{(11)}$	121,8(4)	121,1(4)	$C_{(11)}$—$C_{(12)}$—$C_{(17)}$		120,4(5)
$C_{(9)}$—$C_{(10)}$—$C_{(11)}$	121,4(5)	118,9(5)	$C_{(13)}$—$C_{(12)}$—$C_{(17)}$		120,9(5)
$S_{(2)}$—$C_{(11)}$—$C_{(10)}$	122,4(4)	121,6(4)	$Cl_{(6)}$—$C_{(12)}$—$C_{(11)}$	122,0(4)	
$S_{(2)}$—$C_{(11)}$—$C_{(12)}$	120,6(4)	120,5(4)	$Cl_{(6)}$—$C_{(12)}$—$C_{(13)}$	188,8(4)	

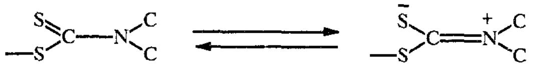


o Id

VII

R = Me, Et; NR2 = morpholino

The molecules have similar structures since the nucleophilic substitution occurs at position 4 of the pyridine ring in both cases. The dithiocarbamate fragments are flat within 0.03 Å and form angles of 77.3 and 85.0° with the planes of the pyridine rings in (IIc) and (IIb) respectively. The bond lengths and valence angles in the dithiocarbamate groups are practically identical and are in good agreement with similar data for other compounds investigated structurally [7]. The intermediate character (between single and double) of the $S_{(1)}$—$C_{(14)}$ bond (1.670 and 1.648 Å) and the marked shortening of the $N_{(8)}$—$C_{(14)}$ distance (1.321 Å) compared to normal, combined with the planar structure of the $S_{(1)}C_{(14)}S_{(2)}N_{(8)}C_{(15)}C_{(16)}$ fragment, indicates the existence of two resonance forms



with a predominant contribution from the second. The existence of identical (within the limits of error of the determination) geometric parameters for this fragment in the different compounds suggests that they represent this electronic structure adequately. The high values for the $C_{(10)}$—$Cl_{(3)}$ and $C_{(12)}$—$Cl_{(6)}$ distances in compound (IIc) of 1.838 and 1.882 Å respectively are worthy of attention. Even in chlorine-substituted cyclohexanes the $C_{(sp^3)}$—Cl bond does not exceed 1.81 Å [8]. The similar bond lengthening is not explained by steric factors since the $C_{(10)}$—$Cl_{(3)}$ (1.713 Å) and $C_{(12)}C_{(17)}$ (1.443 Å) bonds have normal values in the analogous intramolecular contacts in compound (IIc) (Table 1).

The structure of (VII) contains two crystallographically independent molecules. The 1,3-dithiole ring is linked at positions 4 and 5 to pyridine (Fig. 3). The bond lengths and valence angles in the two crystallographically independent molecules are

TABLE 2. Bond Lengths (d) and Valence Angles (ω) in the Two Independent (VII) Molecules

Bond	d, Å	d, Å	Bond	d, Å	d, Å
$Cl_{(1)}$—$C_{(9)}$	1,707(7)	1,710(6)	$N_{(6)}$—$C_{(12)}$	1,308(9)	1,311(8)
$Cl_{(2)}$—$C_{(12)}$	1,734(7)	1,718(6)	$N_{(7)}$—$C_{(13)}$	1,174(9)	1,154(9)
$S_{(3)}$—$C_{(10)}$	1,731(6)	1,714(6)	$C_{(8)}$—$C_{(9)}$	1,409(9)	1,392(9)
$S_{(3)}$—$C_{(14)}$	1,797(7)	1,789(7)	$C_{(8)}$—$C_{(13)}$	1,42(1)	1,438(9)
$S_{(4)}$—$C_{(11)}$	1,733(6)	1,740(6)	$C_{(9)}$—$C_{(10)}$	1,39(1)	1,400(8)
$S_{(4)}$—$C_{(14)}$	1,778(7)	1,769(7)	$C_{(10)}$—$C_{(11)}$	1,366(8)	1,378(8)
$O_{(5)}$—$C_{(14)}$	1,168(9)	1,178(9)	$C_{(11)}$—$C_{(12)}$	1,399(8)	1,392(9)
$N_{(6)}$—$C_{(8)}$	1,335(9)	1,354(8)			

Angle	ω	ω	Angle	ω	ω
$C_{(10)}$—$S_{(3)}$—$C_{(14)}$	95,0(3)	94,3(3)	$C_{(9)}$—$C_{(10)}$—$C_{(11)}$	118,9(6)	116,9(5)
$C_{(11)}$—$S_{(4)}$—$C_{(14)}$	95,7(3)	95,4(3)	$S_{(4)}$—$C_{(11)}$—$C_{(10)}$	117,5(4)	116,2(4)
$C_{(8)}$—$N_{(6)}$—$C_{(12)}$	116,4(6)	117,5(6)	$S_{(4)}$—$C_{(11)}$—$C_{(12)}$	123,9(5)	123,0(5)
$N_{(6)}$—$C_{(8)}$—$C_{(9)}$	124,2(6)	123,3(6)	$C_{(10)}$—$C_{(11)}$—$C_{(12)}$	118,5(5)	120,8(5)
$N_{(6)}$—$C_{(8)}$—$C_{(13)}$	117,5(6)	117,0(6)	$Cl_{(2)}$—$C_{(12)}$—$N_{(6)}$	117,5(5)	118,0(5)
$C_{(9)}$—$C_{(8)}$—$C_{(13)}$	118,3(6)	119,7(6)	$Cl_{(2)}$—$C_{(12)}$—$C_{(11)}$	117,8(5)	119,2(5)
$Cl_{(1)}$—$C_{(9)}$—$C_{(8)}$	121,7(5)	121,1(5)	$N_{(6)}$—$C_{(12)}$—$C_{(11)}$	124,7(6)	122,8(6)
$Cl_{(1)}$—$C_{(9)}$—$C_{(10)}$	121,2(5)	120,3(5)	$N_{(7)}$—$C_{(13)}$—$C_{(8)}$	178,5)7)	178,7(7)
$C_{(8)}$—$C_{(9)}$—$C_{(10)}$	117,1(6)	118,6(5)	$S_{(3)}$—$C_{(14)}$—$S_{(4)}$	113,5(4)	114,5(4)
$S_{(3)}$—$C_{(10)}$—$C_{(9)}$	122,8(5)	123,5(4)	$S_{(3)}$—$C_{(14)}$—$O_{(5)}$	122,1(6)	121,7(6)
$S_{(3)}$—$C_{(10)}$—$C_{(11)}$	118,3(5)	119,5(4)	$S_{(4)}$—$C_{(14)}$—$O_{(5)}$	124,4(6)	123,8(6)

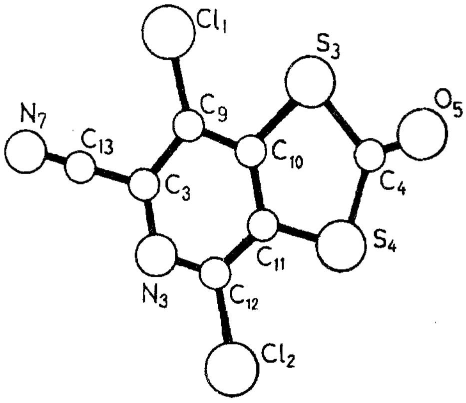


Fig. 3. Structure of 4,7-dichloro-6-cyano-1,3-dithiolo[4,5-c]pyridin-2-one (VII).

the same within the limits of experimental error (Table 2) which indicates the reliability of the results obtained in spite of a low value for the confidence factor.

The bicycle is planar with a precision of 0.02 Å. The mean square deviation from planarity of atoms bonded to the rings does not exceed 0.08 Å. The distance between the sulfur atoms and the carbon atoms of the carbonyl groups and the pyridine rings were markedly different. Thus the mean $S—C_{(pyridine)}$ distance was 1.73 Å while $S—C_{(C=O)}$ was 1.78 Å and was close to the value characteristic of similar bonds with carbon atoms in the sp^3 hybridized state [9]. The difference in bond length of 0.05 Å exceeds by an order of magnitude the error of the determination and, which is significant, occurs in both crystallographically independent molecules. We have no satisfactory explanation for this. The remaining bond lengths in the molecules have standard values. There were no shortened intermolecular contacts in the crystal.

It must be noted that dialkylamine hydrochloride were isolated from the reaction mixture in all cases when the formation of dithiolopyridine derivatives occurred. These initially formed part of the thioamide fragment and enable the formation of compounds

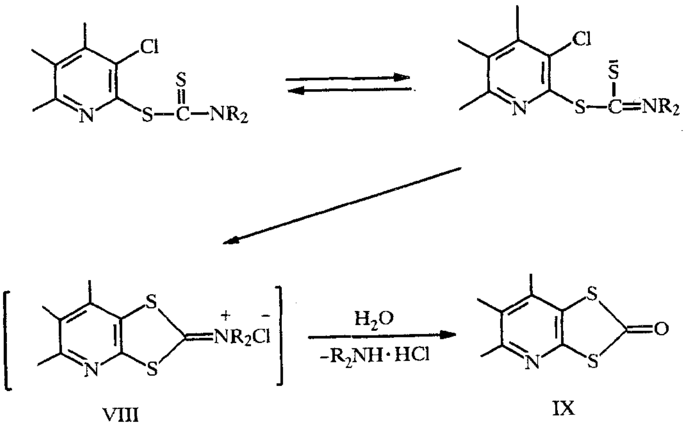
TABLE 3. Atomic Coordinates (× 10^4) of Compound (IIc)

Atom	x	y	z	Atom	x	y	z
$S_{(1)}$	8646(1)	2011(1)	1803(1)	$C_{(15)}$	7125(4)	3295(5)	640(7)
$S_{(2)}$	9665(1)	3936(1)	1159(1)	$C_{(16)}$	8024(4)	4850(4)	266(5)
$Cl_{(3)}$	11274(1)	2373(2)	149(1)	$C_{(17)}$	6490(4)	3734(4)	1502(4)
$Cl_{(4)}$	12471(1)	1252(1)	2028(1)	$C_{(18)}$	5808(3)	4422(5)	1181(9)
$Cl_{(5)}$	10660(1)	2696(1)	5526(1)	$C_{(19)}$	5220(4)	4847(6)	2005(7)
$Cl_{(6)}$	9308(2)	4062(2)	3991(1)	$C_{(20)}$	5320(6)	4590(7)	3142(8)
$N_{(7)}$	11456(2)	2054(3)	3652(4)	$C_{(21)}$	5985(5)	3905(7)	3491(8)
$N_{(8)}$	7994(2)	3751(3)	729(4)	$C_{(22)}$	6589(5)	3500(6)	2710(6)
$C_{(9)}$	11595(3)	1995(4)	2483(5)	$C_{(23)}$	7991(3)	4900(4)	-1041(4)
$C_{(10)}$	11039(3)	2536(5)	1717(6)	$C_{(24)}$	7370(3)	5546(5)	-1589(6)
$C_{(11)}$	10338(8)	3156(3)	2110(5)	$C_{(25)}$	7338(4)	5644(5)	-2787(6)
$C_{(12)}$	10224(4)	3223(4)	3314(6)	$C_{(26)}$	7934(5)	5111(6)	-3449(7)
$C_{(13)}$	10765(3)	2644(3)	4018(4)	$C_{(27)}$	8570(4)	4437(5)	-2936(6)
$C_{(14)}$	8668(4)	3232(4)	1222(4)	$C_{(28)}$	8601(3)	4335(4)	-1726(5)

TABLE 4. Atomic Coordinates (× 10^4) of Compound IIb

Atom	x	y	z	Atom	x	y	z
$S_{(1)}$	-879(1)	-1511(1)	10238(3)	$C_{(10)}$	578(2)	-1571(5)	7165(9)
$S_{(2)}$	-877(1)	-3388(1)	6837(3)	$C_{(11)}$	-26(2)	-2633(5)	8141(9)
$Cl_{(3)}$	505(1)	-801(2)	4827(3)	$C_{(12)}$	80(2)	-3192(5)	10086(9)
$Cl_{(4)}$	2019(1)	79(1)	6912(3)	$C_{(13)}$	766(2)	-2680(4)	10889(9)
$Cl_{(5)}$	922(1)	-3354(1)	13247(2)	$C_{(14)}$	-1271(2)	-2527(4)	8114(9)
$N_{(6)}$	-973(3)	-5164(5)	1214(1)	$C_{(15)}$	-2300(3)	-2216(6)	811(1)
$N_{(7)}$	1342(2)	-1694(4)	9937(7)	$C_{(16)}$	-2200(3)	-3683(6)	522(1)
$N_{(8)}$	-1895(2)	-2835(4)	7200(8)	$C_{(17)}$	-524(3)	-4295(5)	11191(9)
$C_{(9)}$	1241(2)	-1154(5)	808(1)				

(IX) to be represented through the iminium intermediate (VIII) by hydrolysis of the latter by the water molecules contained in the initial dithiocarbamate according to the following scheme:



On the basis of the investigations carried out it has been shown that the formation of the cyclic derivatives (VI) and (VII) by the reaction of polychloropyridines with hydrates of sodium dialkyldithiocarbamates is controlled by the presence of an electron-accepting substituent (more accepting than chlorine atoms, such as a cyano group) and its localization in positions 2 or 4 of the pyridine ring.

TABLE 5. Atomic Coordinates (× 10^4) of Compound (VII)

Atom	*x*	*y*	*z*
$Cl_{(1)}$	0,5626(2)	0,2492(2)	1,2667(1)
$Cl_{(2)}$	0,2737(1)	0,4655(2)	1,0057(1)
$S_{(3)}$	0,6134(2)	0,1642(2)	1,0923(1)
$S_{(4)}$	0,4669(2)	0,2629(2)	0,9669(1)
$O_{(5)}$	0,6345(6)	0,1021(7)	0,9472(3)
$N_{(6)}$	0,3286(5)	0,4375(6)	1,1495(3)
$N_{(7)}$	0,3412(6)	0,4483(7)	1,3456(3)
$C_{(8)}$	0,3906(5)	0,3863(7)	1,2053(4)
$C_{(9)}$	0,4831(5)	0,3048(7)	1,1927(4)
$C_{(10)}$	0,5049(5)	0,2672(6)	1,1171(4)
$C_{(11)}$	0,4396(5)	0,3157(6)	1,0598(3)
$C_{(12)}$	0,3537(5)	0,4021(7)	1,0794(4)
$C_{(13)}$	0,3641(6)	0,4220(7)	1,2820(4)
$C_{(14)}$	0,5831(6)	0,1642(8)	0,9913(4)
$Cl_{(1')}$	-0,0432(2)	0,2886(2)	1,0246(1)
$Cl_{(2')}$	0,2068(2)	-0,0002(2)	0,7664(1)
$S_{(3')}$	-0,1174(2)	0,3301(2)	0,8496(1)
$S_{(4')}$	0,0103(2)	0,1960(2)	0,7248(1)
$O_{(5')}$	-0,1572(6)	0,3550(7)	0,7034(3)
$N_{(6')}$	0,1688(5)	0,0620(6)	0,9091(3)
$N_{(7')}$	0,1787(5)	0,0930(7)	1,1054(3)
$C_{(8')}$	0,1136(6)	0,1274(7)	0,9652(3)
$C_{(9')}$	0,0245(5)	0,2109(7)	0,9511(3)
$C_{(10')}$	-0,0090(5)	0,2305(6)	0,8751(3)
$C_{(11')}$	0,0498(5)	0,1649(7)	0,8190(3)
$C_{(12')}$	0,1376(7)	0,0824(7)	0,8381(3)
$C_{(13')}$	0,1506(6)	0,1074(7)	1,0427(4)
$C_{(14')}$	-0,0991(6)	0,3044(8)	0,7489(4)

EXPERIMENTAL

The IR spectra of compounds was measured on a Specord M 80 instrument in chloroform, NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solution with a Bruker AC 200 instrument with an operating frequency of 200 MHz (PMR) and 50 MHz (^{13}C NMR), internal standard was TMS. Mass spectral measurements were carried out with a Finnegan 4021 instrument (direct insertion, ionization energy 70 eV).

Parameters of unit cells were determined by a photometric method and were refined in a DRON 1.5 diffractometer. The experimental material was obtained on a DAR-UM automatic diffractometer using monochromatic CuKα radiation. Structures were determined by the direct statistical method with subsequent calculation of sets of electron densities. Refinement of the coordinates was effected by an anisotropic full-matrix approach. The poor quality of the crystals obtained did not permit lower R values to be achieved or H atoms to be localized in compounds (IIb) and (IIc). Atomic coordinates are given in Tables 3-5.

2,3,5,6-Tetrachloro-4-pyridyl N,N-Dimethyldithiocarbamate (IIa) $C_8H_6Cl_4N_2S_2$. Sodium dimethyldithiocarbamate dihydrate (0.013-0.015 mole) was added with stirring at room temperature to a solution of compound (Ia) (0.01 mole) in acetone (50-70 ml). The reaction mixture was stirred for 3-5 h. The precipitate of NaCl was removed by filtration. The solvent was evaporated, the residue washed with water, extracted with chloroform, the extract dried, and the solvent evaporated. The product was recrystallized from methanol or benzene. The yield of yellow crystals of mp 166-168°C (methanol) was 89%. Found: $[M-Cl]^+$ 299. IR spectrum: 1510, 1525 cm^{-1} (C=S). PMR spectrum: 3.44 and 3.51 ppm (3H, s, NMe_2). ^{13}C NMR: 42.4 and 45.4 (2s, NMe_2), 136.4 (s, $C_{(3)}$, $C_{(5)}$), 144.8 (s, $C_{(4)}$), 146.3 (s, $C_{(2)}$, $C_{(6)}$), 187.7 ppm (s, C=S).

TABLE 6. Crystallographic Parameters

Parameter	(IIc) $C_{20}H_{14}N_2Cl_4S_2$	(IIb) $C_9H_4N_3Cl_3S_2$	VII $C_7Cl_2N_2OS_2$
u, Å	15,249 (6)	21,573 (7)	11,706 (5)
b	12,532 (5)	11,699 (5)	9,177 (5)
c	11,435 (5)	5,979 (3)	17,443 (6)
γ	87,8(1)	120,7 (2)	97,25 (5)
V, Å	2183,6	1297,5	1858,9
M	417,4	324,6	263,1
Z	4	4	8
d_{calc}, g/cm^3	1,277 i	1,671	1,891
Space group	P $2_{1/n}$	P $2_{1/a}$	P $2_{1/a}$
No. of reflections	1878	1449	2055
R Factor	0,082	0,064	0,072

2,3,5,6-Tetrachloro-4-pyridyl N,N-Dibenzyldithiocarbamate (IIc) $C_{20}H_{14}N_2Cl_4S_2$ was obtained in a similar manner to compound (IIa) using sodium dibenzyldithiocarbamate. The yield of yellow crystals of mp 149-150°C (hexane) was 80%. Found: $[M-Cl]^+$ 451. IR spectrum: 1510, 1525 cm^{-1} (C=S). ^{13}C NMR spectrum: 55.6, 56.2 (2s, $2CH_2$), 121.1-129.3 m, 133.7 s, 134.7 s ($2C_6H_5$), 136.3 (s, $C_{(3)}$, $C_{(5)}$), 144.8 (s, $C_{(4)}$), 146.3 (s, $C_{(2)}$, $C_{(6)}$), 189.9 ppm (s, C=S).

Reaction of Compound (Ib) with Sodium Dimethyldithiocarbamate Dihydrate. The reagent (0.0075 mole) was added with stirring at room temperature to a solution of compound (Ib) (1.21 g: 0.005 mole) in acetone (50 ml) and the reaction mixture stirred for 2-3 h. A yellow solid was precipitated which was filtered off, washed on the filter with water, then with acetone, and dried. Compound (III) (0.7 g) was obtained. The filtrate was evaporated, washed with water, and dried. The residue was chromatographed on a column of silica gel (eluent was benzene). Compound (IIb) (0.81 g) and more of compound (III) (0.16 g) were obtained.

2,5,6-Trichloro-3-cyano-4-pyridyl N,N-Dimethyldithiocarbamate (IIb) $C_9H_4N_3Cl_3S_2$. Yellow crystals of mp 150-151°C (methanol). Found: $[M-Cl]^+$ 290. IR spectrum: 1510, 1520 cm^{-1} (C=S). PMR spectrum: 3.40 (3H, s), 3.52 ppm (3H, s, NMe_2). ^{13}C NMR: 42.9 and 45.4 (2s, NMe_2), 112.7 (s, CN), 118.0 (s, $C_{(3)}$), 136.5 (s, $C_{(5)}$), 148.6 (s, $C_{(4)}$), 149.6 (s, $C_{(2)}$), 152.7 (s, $C_{(6)}$), 188.9 ppm (s, C=S).

3,6-Dichloro-5-cyano-2,4-bis(N,N-dimethyldithiocarbamato)pyridine (III) $C_{12}H_6Cl_2N_4S_4$. Yellow crystals of mp 200°C (with decomposition, benzene). IR spectrum: 1510, 1525 cm^{-1} (C=S). PMR spectrum: 3.49, 3.55 ppm (6H, s, NMe_2). ^{13}C NMR spectrum: 42.9, 43.8, 44.8, 45.4 (4s, $2NMe_2$), 113.1 (s, CN), 117.5 (s, $C_{(5)}$), 139.5 (s, $C_{(3)}$), 147.0 (s, $C_{(4)}$), 150.2 (s, $C_{(6)}$), 158.2 (s, $C_{(2)}$), 186.8, 187.5 ppm (s, C=S).

Reaction of Compound (Ic) with Sodium Dimethyldithiocarbamate Dihydrate. A. The reagent (0.72 g: 0.004 mole) dissolved in acetone (50 ml) was added to a solution of compound (Ic) (0.484 g: 0.002 mole) in acetone (40 ml) with stirring at room temperature. The reaction mixture was stirred for 3 h, filtered, evaporated, the residue washed with water, and extracted with chloroform. The extract was dried, evaporated, and the residue chromatographed on a column of silica gel (eluent was benzene—ethyl acetate, 15:1). Compound (IV) (0.7 g: 85%) was obtained.

B. The reaction mixture obtained in a similar way to example **A** was boiled for 12 h, and then treated as in **A**. The reaction mixture was chromatographed on a column of silica gel (eluent was benzene—hexane, 2:1). Compound (V) (0.18 g: 10%) and compound (VI) (0.69 g: 44%) were obtained.

C. Compound (IV) (0.2 g: 0.00049 mole) was boiled in acetone (20 ml) for 10 h. Treatment was then analogous to example **A**, the eluent being benzene. Compound (VI) (0.07 g: 50%) and compound (V) (0.017 g: 10%) were obtained.

D. Compound (V) (0.1 g: 0.00029 mole) was boiled in acetone (10 ml) for 8 h. Treatment was then analogous to example **C**. Compound (VI) (0.048 g: 70%) was obtained.

3,5-Dichloro-4-cyano-2,6-bis(N,N-dimethyldithiocarbamato)pyridine (IV) $C_{12}H_6Cl_2N_4S_4$. Yellow crystals of mp 179°C. IR spectrum: 1505, 1520 cm^{-1} (C=S). PMR spectrum: 3.67, 3.68, 3.70, 3.73 ppm (12H, 4s, $2NMe_2$). ^{13}C NMR: 42.6, 43.2, 44.9, 45.6 (4s, $2NMe_2$), 113.0 (s, CN), 132.0 and 132.8 (2s, $C_{(3)}$, $C_{(5)}$), 137.7 (s, $C_{(4)}$), 154.0, 154.8 (2s, $C_{(2)}$, $C_{(6)}$), 187.4, 188.1 ppm (2s, C=S).

6-Chloro-7-cyano-5-(N,N-dimethyldithiocarbamato)-1,3-dithiolo[4,5-b]pyrid-2-one (V) $C_{12}H_6ClN_3OS_4$. Yellow crystals of mp 128-129°C. Found: $[M-Cl]^+$ 312. IR spectrum: 1505, 1520 cm^{-1} (C=S), 1700, 1720 cm^{-1} (C=O). PMR spectrum: 3.67, 3.68 ppm (6H, 2s, NMe_2). ^{13}C NMR: 42.4, 45.2 (2s, NMe_2), 113.3 (s, CN), 124.0 (s, $C_{(4)}$), 129.1 (s, $C_{(7)}$). 133.1 (s, $C_{(6)}$), 154.5 (s, $C_{(8)}$), 156.4 (s, $C_{(5)}$), 183.3 (s, $C_{(2)}$), 188.4 ppm (s, C=S).

8-Cyanobis-1,3-dithiolo[4,5-b:4′,5′-e]pyridine-2,6-dione (VI) $C_8N_2O_2S_4$. Yellow crystals of mp 204-205°C. Found: M^+ 284. IR spectrum: 1700, 1710 cm^{-1} (C=O). ^{13}C NMR: 108.4 (s, $C_{(3')}$, $C_{(4')}$), 113.9 (s, CN), 131.3 (s, $C_{(8)}$), 152.4 (s, $C_{(7')}$, $C_{(8')}$), 183.1 ppm (s, $C_{(2)}$, $C_{(6)}$).

4,7-Dichloro-6-cyano-1,3-dithiolo[4,5-c]pyrid-2-one (VII) $C_7Cl_2N_2OS_2$. A solution of sodium N,N-dimethyldithiocarbamate, sodium N,N-diethyldithiocarbamate, or sodium N-morpholinodithiocarbamate dihydrate (0.02 mole) in acetone was added with stirring at room temperature to a solution of compound (IId) (2.42 g: 0.01 mole) in acetone (70 ml). The reaction mixture was stirred for 2 h at room temperature, filtered, and evaporated. The residue was chromatographed on a column of silica gel (eluent was benzene—hexane, 1:2). Compound (VII) (2.18 g: 83%) was obtained as white crystals of mp 121-122°C (hexane). Found: M^+ 262. IR spectrum: 1690, 1760 cm^{-1}. ^{13}C NMR: 113.0 (s, CN), 128.1 (s, $C_{(2)}$), 128.7 (s, $C_{(5)}$), 134.6 (s, $C_{(3)}$), 142.0 (s, $C_{(4)}$), 145.4 (s, $C_{(6)}$), 182.0 ppm (s, C=O).

Crystals of compounds (IIb), (IIc), and (VII) were monoclinic with the crystallographic parameters shown in Table 6.

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