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HEXAHYDROBENZOTHIAZOLO[3,2-a]PYRIDINIUM SALTS

A. M. Shestopalov, V. N. Nesterov,
Yu. A. Sharanin, V. P. Litvinov,
V. E. Shklover, Yu. T. Struchkov,
and V. K. Promonenkov

UDC 547.821.3'789.6.04:
548.737:543.422.25:
541.634

Salts of hexahydrobenzothiazolo[3,2-a]pyridine are obtained by exchange reactions. Anions are placed in the order $[(NC)_2CCHC(CN)_2]^- > ClO_4^- > I_3^- > Br^-$ according to the ability to displace each other. X-ray structural and spectroscopic studies establish the cis-attachment of the thiazolidine and cyclohexane rings in the hexahydrobenzothiazolo[3,2-a]pyridinium salts studied.

Electrophilic quaternization of 2-N-, O-, S-, and Se-allylpyridines is a convenient method for synthesis of annelated heterocycles which are useful in practice [1-3]. Quaternization of 2-[2-cyclohexen-1-ylthio(seleno)]pyridines by reaction with halogens occurs as an electrophilic intramolecular trans-quaternization with formation of 4a,10a-cis-4,4a-trans-1,2,3,4,4a,10a-hexahydrobenzothiazolo(selenazolo)[3,2-a]pyridinium salts [1]. In this work, the reaction of hexahydrobenzothiazolo[3,2-a]pyridinium salts with electrophilic and nucleophilic reagents is studied and some stereochemical aspects of this reaction are given.

The tribromide I in the absence of benzothiazolo[3,2-a]pyridinium triiodide II is shown to react with acetone. During this the tribromide I is converted into bromide III and the acetone into bromoacetone IV. The bromination of acetone proceeds with 72% yield of the final product IV even with heterogeneous phases at room temperature. Addition of an equivalent quantity of bromine to a suspension of benzothiazolo[3,2-a]pyridinium bromide III in chloroform again leads to the tribromide I. The bromide III plays a catalytic role.

The reaction of salts I-III with perchloric acid, iodine, potassium 1,1,3,3-tetracyanopropenide (VII) was also studied. Treatment of salts I-III with perchloric acid with heating in acetic acid leads to benzothiazolo[3,2-a]pyridinium perchlorates V and VI.

Heating bromide III in acetic acid with an excess of potassium iodide and iodine together with exchange of bromide for triiodide substitutes the bromine by iodine in the cation of the starting salt. However, the 1,1,3,3-tetracyanopropenide anion is more active in the exchange reactions.

The ability to displace the anions from the hexahydrobenzothiazolo[3,2-a]pyridinium salts depends on the nature of the conjugate base and is related to the strength of the corresponding acid. Thus, the tetracyanopropenide VIII and the perchlorate V are obtained from the tribromide I with yields of 86 and 78%, respectively. The bromide III is converted into the perchlorate V with an 85% yield. Besides this, the bromide III and perchlorate V upon

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T. G. Shevchenko Voroshilovgrad State Pedagogical Institute, Voroshilovgrad 348011. N. D. Zelinskií Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow 117913. A. N. Nesmeyanov Institute of Organometallic Compounds, Academy of Sciences of the USSR, Moscow 117813. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1682-1688, December, 1988. Original article submitted May 19, 1987; revision submitted November 20, 1987.

TABLE 1. Hexahydrobenzothiazolo[3,2-a]pyridinium Salts III, VI, and VIII

Compound	T_{mp}, °C	IR spectrum, cm^{-1} C≡N	NMR spectrum, δ, ppm (in DMSO-D_6), c.c., Hz									Calc. torsion angle		Found, %					Structural formula	Calculated %					Yield %
			8-CH_3 (s)	6-CH_3 (s)	CH—Hal (m)	CH—S (m)	CH—N (d.d)	C'H (s)	$(CH_2)_3$ (m)	$^3J_{cis}$	$^3J_{trans}$	$\varphi\ H_aH_b$	$\varphi\ H_aH_c$	C	H	Hal	N	S		C	H	Hal	N	S	
III	162	2235	2,66	3,08	4,83	5,11	6,19	7,88	1,75, 2,09, 2,34	5,3	9,9	51	148	41,3	3,7	39,2	6,6	8,0	$C_{14}H_{16}Br_2NS$	41,6	4,0	39,5	6,9	7,9	92
VI	231	2237	2,67	3,12	4,79	5,02	6,09	7,84	1,73, 2,07, 2,33	5,1	10,6	53	152	35,3	3,2	34,1*	5,7	6,7	$C_{14}H_{15}ClN_2O_4S$	35,7	3,4	34,5	6,0	6,8	85
VIII	158...159	2235, 2185, 2190, 2215	2,68	3,06	4,82	5,03	6,08	7,81, 7,20 (CH анио-на)	1,77, 2,06, 2,33**	5,1	9,9	53	148	54,0	3,5	16,8	17,7	6,7	$C_{21}H_{17}BrN_6S$	54,2	3,7	17,2	18,0	6,9	86**

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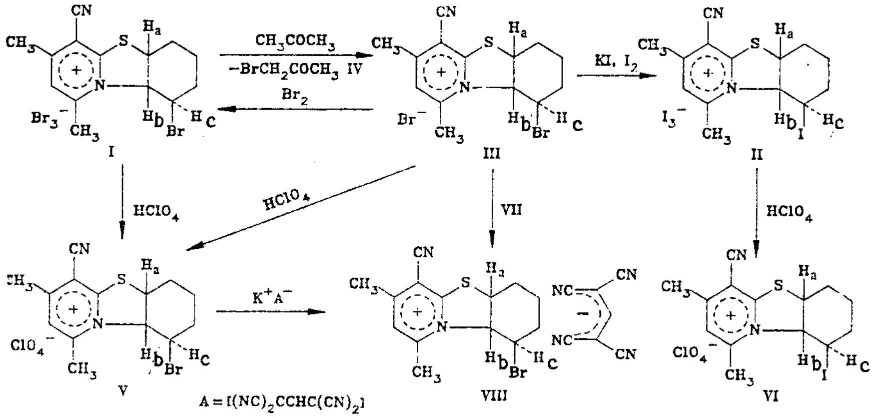
*Total.

**Calculated for bromide III.

TABLE 2. Bond Angles, ω, in the Structure of VIII

Angle	ω°	Angle	ω°	Angle	ω°
$C_{(10a)}C_{(1)}C_{(2)}$	112,9(3)	$C_{(7)}C_{(6)}C_{(14)}$	122,9(3)	$C_{(1)}C_{(10a)}C_{(4a)}$	115,2(3)
$C_{(1)}C_{(2)}C_{(3)}$	110,1(4)	$C_{(6)}C_{(7)}C_{(8)}$	123,9(3)	$C_{(9)}C_{(11)}N_{(12)}$	178,8(4)
$C_{(2)}C_{(3)}C_{(4)}$	110,4(3)	$C_{(7)}C_{(8)}C_{(9)}$	116,5(3)	$C_{(16)}C_{(15)}C_{(20)}$	124,8(3)
$C_{(3)}C_{(4)}C_{(4a)}$	110,7(3)	$C_{(7)}C_{(8)}C_{(13)}$	122,2(4)	$C_{(16)}C_{(15)}C_{(21)}$	120,7(3)
$C_{(3)}C_{(4)}Br$	109,5(3)	$C_{(9)}C_{(8)}C_{(13)}$	121,2(4)	$C_{(20)}C_{(15)}C_{(21)}$	114,5(3)
$BrC_{(4)}C_{(4a)}$	112,7(3)	$C_{(8)}C_{(9)}C_{(9a)}$	120,0(3)	$C_{(15)}C_{(16)}C_{(17)}$	129,7(3)
$C_{(4)}C_{(4a)}C_{(10a)}$	110,9(3)	$C_{(8)}C_{(9)}C_{(11)}$	121,0(3)	$C_{(16)}C_{(17)}C_{(18)}$	124,1(4)
$C_{(4)}C_{(4a)}N_{(5)}$	111,2(3)	$C_{(9a)}C_{(9)}C_{(11)}$	119,0(3)	$C_{(16)}C_{(17)}C_{(19)}$	121,3(3)
$C_{(10a)}C_{(4a)}N_{(5)}$	104,7(3)	$C_{(9)}C_{(9a)}N_{(5)}$	120,4(3)	$C_{(18)}C_{(17)}C_{(19)}$	114,6(3)
$C_{(4a)}N_{(5)}C_{(6)}$	126,0(3)	$S_{(10)}C_{(9a)}N_{(5)}$	113,5(2)	$N_{(1)}C_{(18)}C_{(17)}$	177,7(4)
$C_{(4a)}N_{(5)}C_{(9a)}$	122,3(2)	$S_{(10)}C_{(9a)}C_{(9)}$	126,0(2)	$N_{(2)}C_{(19)}C_{(17)}$	178,2(4)
$C_{(6)}N_{(5)}C_{(9a)}$	121,7(3)	$C_{(9a)}S_{(10)}C_{(10a)}$	89,3(1)	$N_{(3)}C_{(20)}C_{(15)}$	178,4(4)
$N_{(5)}C_{(6)}C_{(7)}$	117,2(3)	$S_{(10)}C_{(10a)}C_{(1)}$	114,0(3)	$N_{(4)}C_{(21)}C_{(15)}$	176,5(4)
$N_{(5)}C_{(6)}C_{(14)}$	119,6(3)	$S_{(10)}C_{(10a)}C_{(4a)}$	102,5(2)		

reaction with compound VII in methanol at 25-40°C form the salt VIII with yields of 89 and 83%, respectively. The anions are placed in the order $[(NC)_2CCHC(CN)_2]^- > ClO_4^- > I_3^- > Br^-$ according to the ability to displace each other, which corresponds with the literature data for other reactions of anion exchange [4, p. 103]. The x-ray structural analysis shows the effect of significant delocalization of the negative charge in the anion on the stability of compound VIII.



IR and NMR spectra of hexahydrobenzothiazolo[3,2-a]pyridinium salts I [1], II, III, V, VI, and VIII show that the conversion discussed above does not change the conformation of the cation (Table 1 and 2). In the IR spectra of the these salts, a weak absorption band of the CN group occurs in the region 2235-2237 cm^{-1} which is characteristic for quaternized azines [1, 3]. The absorption bands of the CN group in the 1,1,3,3-tetracyanopropenide in the IR spectrum of VIII appear at 2185, 2190, and 2215 cm^{-1}, which is consistent with the ionic character of VIII. In the NMR spectra of the salts I-III, V, VI, and VIII, a characteristic shift of the proton signals of the C^7H, 8-CH_3, and 6-CH_3 groups to weak field at 7.81-7.88, 2.66-2.68, and 3.06-3.08 ppm, respectively, is observed by comparison with the starting 2-(2-cyclohexen-1-ylthio)pyridines [1]. The multiplicity of the $SCH_aCH_bCH_cHal$ group protons of III, VI, and VIII is analogous to the multiplicity of the corresponding protons of earlier obtained hexahydrobenzothiazolo[3,2-a]pyridinium salts I, II, and V [1]. The cis- and trans-location of atoms H_a and H_b, $^3J_{cis}$ 5.1-5.3 Hz, and also atoms H_b and H_c, $^3J_{trans}$ 9.9-10.6 Hz, is preserved. The calculated values of the dihedral angles φH_aH_b and φH_bH_c for compounds III, IV, and VII (Table 1) relative to Karplus-Conroy [5, p. 122] support the correct assignment of the coupling constants and agree well with the corresponding values obtained earlier for hexahydrobenzothiazolo[3,2-a]pyridinium salts [1] and also with data from the x-ray structure of VIII.

The x-ray structure study of VIII was carried out for unambiguous establishment of the structure of the reaction products from electrophilic quaternization of substituted 2-[2-cyclohexen-1-ylthio(seleno)]pyridine and further study of the stereochemistry of this reaction.

TABLE 3. Torsion Angles, τ, in the Thiazolidine Heterocycle and Cyclohexane Ring in the Cation of VIII

Angle	τ°	Angle	τ°	Angle	τ°
$S_{(10)}C_{(10a)}C_{(4a)}N_{(5)}$	−42,4(3)	$C_{(9a)}S_{(10)}C_{(10a)}C_{(4a}$	33,0(4)	$C_{(3)}C_{(4)}C_{(4a)}C_{(10a)}$	53,5(5)
$C_{(10a)}C_{(4a)}N_{(5)}C_{(9a)}$	35,2(4)	$C_{(10a)}C_{(1)}C_{(2)}C_{(3)}$	−52,2(5)	$C_{(4)}C_{(4a)}C_{(10a)}C_{(1)}$	−46,8(4)
$C_{(4a)}N_{(5)}C_{(9a)}S_{(10)}$	−9,5(3)	$C_{(1)}C_{(2)}C_{(3)}C_{(4)}$	60,0(5)	$C_{(4a)}C_{(10a)}C_{(1)}C_{(2)}$	47,2(5)
$N_{(5)}C_{(9a)}S_{(10)}C_{(10a)}$	−14,6(4)	$C_{(2)}C_{(3)}C_{(4)}C_{(4a)}$	−61,0(5)		

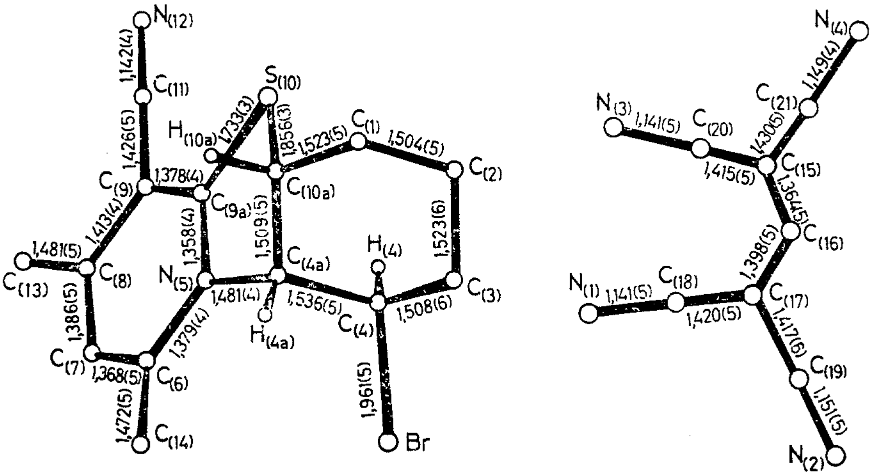


Fig. 1. Molecular structure of VIII. Only hydrogen atoms which show the cis-attachment of the thiazolidine and cyclohexane rings and the trans-location of $H_{(4)}$ and $H_{(4a)}$ are shown.

Compound VIII is the 1,1,3,3-tetracyanopropenide $[C_7HN_4]^-$ of 4-bromo-6,8-dimethyl-9-cyano-1,2,3,4,4a,10a-hexahydrobenzothiazolo[3,2-a]pyridine $[C_{14}H_{16}BrN_2S]$.

The bond and torsion angles in the anion and cation of VIII are given in Tables 2 and 3. Figure 1 shows the overall view with bond lengths.

The thiazolidine heterocycle of the cation has the twist conformation (modified parameters [6] of Cremer–Pole [7] are φ_2 = 178.0° and q_2 = 0.570 Å). An analogous conformation of this heterocycle occurs in earlier studied structures of 3-bromomethyl-2,3-dihydro-5,7-dimethyl-8-cyanothiazolo[3,2-a]pyridinium perchlorate (IX) [3] and 4-iodo-6,8-dimethyl-9-cyano-1,2,3,4,4a,10a-hexahydrobenzothiazolo[3,2-a]pyridinium triiodide (II) [1], although in cis-2,3-(3'-cyclohexanon-1'2'-ylen)-5-methyl-8-ethoxydihydrothiazolo[3,2-a]pyridine [8] and in 2-(2,6-dimethylphenyl)-imino-3-(2-methylbenzoyl)thiazolidine (XI) [9] the opposite conformation is found.

As in II and X, the thiazolidine ring in VIII has a cis-attachment with the cyclohexane ring (torsion angle $H_{(4a)}$ $C_{(4a)}C((_{10a})H_{(10a)}$ is −53(5)°) but the trans-location of the $H_{(4)}$ and $H_{(4a)}$ atoms (torsion angle $H_{(4)}C_{(4)}C_{(4a)}H_{(4a)}$ is 167(5)°) shows that the electrophilic heterocyclization of 2-[2-cyclohexen-1-ylthio(seleno)]pyridines in benzothiazolo[3,2-a]pyridine salts occurs as a trans-process. The substituted cyclohexane ring has a distorted chair conformation (Table 3). As in cation II, the distortion of the conformation of this ring in VIII apparently is caused by shortened nonbonded contacts between the equatorial substituents: the bromine atom (in II, the iodone) at distance Br—$N_{(5)}$ 3.354(5) and Br—$C_{(14)}$ 3.524(5) Å (with the sum of Van der Waals radii of 3.4 Å for Br—N and 3.55 Å for Br—C [10]), and also by the contacts $S_{(10)}$—$C_{(2)}$ and $S_{(10)}$—$C_{(4)}$ at distances 3.387(3) and 3.206(3) Å (with the sum of Van der Waals radii of 3.5 Å for S—C [10]), while in X similar steric problems are absent. The equatorial position of the bromine is characterized by the torsion angles $BrC_{(4)}C_{(3)}C_{(2)}$, 174.1(5°), and $BrC_{(4)}C_{(4a)}C_{(10a)}$, 176.6(4)°.

In VIII as in II, the pyridine heterocycle is not completely planar and has a distorted conformation: atom N(5) deviates from the plane of the remaining five atoms (the deviation of which from the mean plane do not exceed 0.007(5) Å) by −0.066(3) Å. The disruption of the

TABLE 4. Atomic Coordinates (× 10^5 for Br and S; × 10^4 for N and C; × 10^3 for H) in VIII

Atom	x	y	z	Atom	x	y	z
Br	39710(8)	25983(3)	27919(4)	$C_{(17)}$	3483(6)	4897(2)	7836(3)
$S_{(10)}$	−225(2)	42106(6)	41249(7)	$C_{(18)}$	3020(7)	4395(3)	8473(3)
$N_{(1)}$	2617 (7)	4007(3)	9002(3)	$C_{(19)}$	3463(7)	5545(3)	8205(3)
$N_{(2)}$	3416(8)	6066(3)	8522(4)	$C_{(20)}$	3582(7)	3573(2)	6807(3)
$N_{(3)}$	3242(8)	3062(2)	7085(3)	$C_{(21)}$	4464(7)	4190(2)	5480(3)
$N_{(4)}$	4851(6)	4149(2)	4715(3)	$H_{(1,1)}$	−199(5)	258(2)	419(3)
$N_{(5)}$	772(5)	3783(2)	2523(2)	$H_{(1,2)}$	−227(5)	311(2)	490(2)
$N_{(12)}$	1011(7)	5980(2)	3700(3)	$H_{(2,1)}$	88(6)	302(2)	532(3)
$C_{(1)}$	−1439(6)	2910(2)	4498(3)	$H_{(2,2)}$	24(9)	228(3)	558(4)
$C_{(2)}$	302(8)	2664(2)	4992(3)	$H_{(3,1)}$	101(5)	203(2)	395(3)
$C_{(3)}$	1606(8)	2396(2)	4286(4)	$H_{(3,2)}$	256(7)	221(2)	453(3)
$C_{(4)}$	2096(6)	2929(2)	3608(3)	$H_{(4)}$	248(5)	330(2)	383(2)
$C_{(4a)}$	367(6)	3182(2)	3061(3)	$H_{(4a)}$	−2(4)	289(2)	272(2)
$C_{(6)}$	1185(6)	3805(2)	1596(3)	$H_{(7)}$	193(7)	438(2)	65(3)
$C_{(7)}$	1661(7)	4404(2)	1243(3)	$H_{(10a)}$	−224(5)	351(2)	335(3)
$C_{(8)}$	1705(6)	4985(2)	1753(3)	$H_{(13,1)}$	311(8)	549(3)	100(4)
$C_{(9)}$	1171(6)	4941(2)	2684(3)	$H_{(13,2)}$	286(7)	587(2)	171(4)
$C_{(9a)}$	680(5)	4340(2)	3046(3)	$H_{(13,3)}$	124(9)	593(3)	130(4)
$C_{(10a)}$	−1082(6)	3393(2)	3715(3)	$H_{(14,1)}$	145(7)	287(2)	124(3)
$C_{(11)}$	1068(6)	5515(2)	3253(3)	$H_{(14,2)}$	116(6)	336(2)	43(3)
$C_{(13)}$	2142(7)	5629(3)	1331(4)	$H_{(14,3)}$	−59(9)	312(3)	99(4)
$C_{(14)}$	918(8)	3212(3)	1013(3)	$H_{(16)}$	418(5)	517(2)	659(3)
$C_{(15)}$	3995(6)	4199(2)	6436(3)				
$C_{(16)}$	3929(6)	4780(2)	6915(3)				

planarity of the pyridine ring in VIII and II is explained by the steric problems indicated above concerning the bromine atom (in II, the iodine atom). In the cation of IX and X, the pyridine heterocycle is strictly planar.

Steric interaction of the cyano group $C_{(11)}{\equiv}N_{(12)}$ with the $S_{(10)}$ atom and the $C_{(13)}H_3$ group causes deviations of the $S_{(10)}$, $C_{(11)}$, and $C_{(13)}$ atoms from the planar fragment of the pyridine ring by 0.180(1), 0.066(4), and 3.093(3); $C_{(11)}$–$C_{(13)}$, 2.913(5) Å (with the sum of Van der Waals radii of 3.5 for S–C and 3.4 Å for C–C [10]).

The bond length $S_{(10)}$–$C_{(9a)}$ of 1.733(3) Å is shortened by comparison with the standard value for the length of an ordinary S–$C_{(sp^2)}$ of 1.77 Å [9] (1.736(3) Å in II, 1.737(6) Å in IX, and 1.722(5) Å in X), while in XI the S–C length is markedly longer and equal to 1.772(5) Å. The bond length $S_{(10)}$–$C_{(10a)}$ of 1.856(3) Å is increased by comparison with the standard bond length of S–$C_{(sp^3)}$ of 1.817 Å [11], and also with the length of the corresponding bond in IX (1.809(7) Å) and XI (1.796(7) Å) and practically coincides with the 1.850(4) Å length in II and 1.844(5) Å in X. Closure of the thiazolidine heterocycle and its cis-attachment with the cyclohexane ring, to which the electrophilic quaternization of the substituted 2-(2-cyclohexen-1-ylthio)-pyridines leads, causes steric strain in the cyclic fragments of the cation of VIII, appearing (besides the conformational features indicated above) also in the deformation of these fragments (decrease in the bond angles $S_{(10)}C_{(10a)}C_{(4a)}$ to 102.5(2)° and $C_{(10a)}C_{(4a)}N_{(5)}$ to 104.7(3)°) and in the increase of the $S_{(10)}$–$C_{(10a)}$ bond length. Analogous changes are seen in the cations of II and X with similar structure of mechanism of formation.

The bond distances and angles in the pyridine heterocycle are near those observed in II, IX, and X.

The tetracyanopropenide anion has an approximately planar structure (deviations of atoms from the plane of the anion do not exceed 0.039(5) Å, Fig. 1). The planar structure of the anion is explained by the delocalization of the negative charge. Thus, the length of the formally double bond $C_{(15)}{=}C_{(16)}$, 1.364(5) Å, is increased while the length of the formally single bond $C_{(16)}$–$C_{(17)}$, 1.398(5) Å, is greatly shortened (standard length $C_{(sp^2)}{=}C_{(sp^2)}$, 1.333 Å and $C_{(sp^2)}$–$C_{(sp^3)}$, 1.507 Å [12, p. 431]). The bond lengths $C_{(sp^2)}$–$C_{(sp)}$ and C≡N have usual values [12, p. 198] and are equal to 1.415(5)-1.430(5) and 1.141(5)-1.151(5) Å, respectively. The shortened nonbonding $C_{(18)}$–$C_{(20)}$, 2.960(2)Å, (with the sum of Van der Waals radii of 3.4 Å [10]) explains the significant increase in the bond angle $C_{(15)}C_{(16)}C_{(17)}$ to 129.7(3)° and also the angles $C_{(16)}C_{(15)}C_{(20)}$ to 124.8(3)° and $C_{(16)}C_{(17)}C_{(18)}$ to 124.1(4)°.

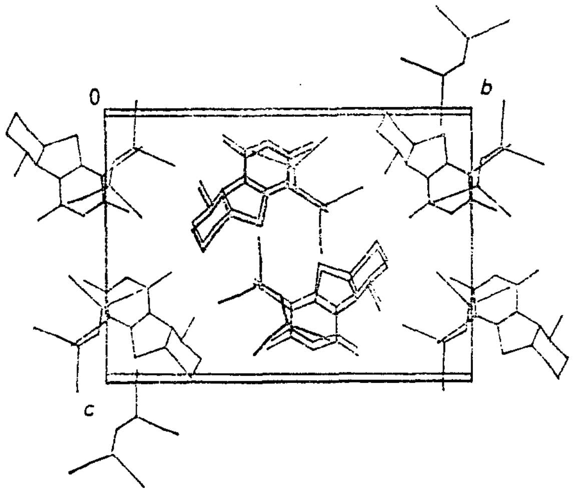


Fig. 2. Projection on bc of the unit cell of VIII. The cation and anion of the asymmetric unit are defined by thick lines.

In the crystal of VIII, the alternating cations and anions form stacks along the a axis (Fig. 2). In the stacks, each anion is pressed between pyridine rings of the two cations which are almost parallel to it at interplanar distances of 3.48-3.79 Å.

EXPERIMENTAL

IR spectra of the compounds were recorded on a UR-20 instrument as KBr tablets. NMR spectra were recorded on a Bruker WM-250 (250 MHz) instrument in DMSO-D_6 (TMS internal standard).

Crystals of VIII are monoclinic: $a = 7.275(3)$, $b = 20.274(3)$, $c = 14.249(2)$ Å, $\beta = 92.91(2)°$, $V = 2113.6$ Å^3, $d_{calc} = 1.46$ g/cm^3, $z = 4$ $[C_{14}H_{16}BrN_2S]^+[C_7HN_4]^{2-}$, space group $P2_1/n$. Unit cell parameters and intensities of 2041 independent reflections with $F^2 > 5\sigma$ were measured on a 4-circle automatic Enraf-Nonius CAD 4 diffractometer (20°C, $\lambda_{MoK\alpha}$, graphite monochromator, relative scanning rate $\omega:\theta = 1.2:1.2$, $\theta_{max} = 53°$). The structure was solved by the heavy atom method. The hydrogen atoms were located in a difference Fourier map. The nonhydrogen atoms were refined by anisotropic full matrix least squares methods, the hydrogen atoms were refined isotropically. The final agreement factors were $R = 0.045$ and $R_w = 0.056$. All calculations were carried out on an IBM PDP 11/23 using programs SDP-PLUS [14]. The atomic coordinates are given in Table 4. The isotropic equivalent temperature factors for the nonhydrogen atoms (for H atoms, isotropic) can be obtained from the authors.

4-Bromo-6,8-dimethyl-9-cyano-4a,10a-cis-4,4a-trans-1,2,3,4,4a,10a-hexahydrobenzothiazolo[3,2-a]pyridinium Bromide (III). To 15 ml acetone with stirring was added in small portions 2.8 g (5 mmole) of I [1]. The reaction mixture was stirred for 20 min at 25°C. The precipitate was filtered, washed with acetone, and 1.86 g (92%) of III was obtained.

4-Bromo-6,8-dimethyl-9-cyano-4a,10a-cis-4,4a-trans-1,2,3,4,4a,10a-hexahydrobenzothiazolo[3,2-a]pyridinium Tribromide (I). To a suspension of 1.2 g (3 mmole) of III monobromide in 15 ml of chloroform with stirring was added over 10 min at 25°C a solution of 0.15 ml (3 mmole) of bromine in 5 ml chloroform. The reaction mixture was stirred for 30 min, the precipitate was filtered, washed with chloroform and ether. The yield of I was 1.3 g (78%). The product was identified as the tribromide, described in [1].

Bromoacetone (IV). To a suspension of 0.4 g (1 mmole) of III in 20 ml acetone was added 2.55 ml (50 mmole) of bromine at 25°C over 20 min. The reaction mixture was stirred for 30 min and the precipitate of III was filtered. The excess acetone was evaporated from the filtrate. Then the bromoacetone was distilled at reduced pressure, the fraction boiling at 42°C (20 mm Hg std.) being collected, 4.9 g (72%) yield.

6,8-Dimethyl-9-cyano-4-iodo-4a,10a-cis-4,4a-trans-1,2,3,4,4a,10a-hexahydrobenzothiazolo-[3,2-a]pyridinium Triiodide (II). A mixture of 0.4 g (1 mmole) III, 0.51 g (2 mmole) iodine, and 0.33 g (2 mmole) potassium iodide in 10 ml acetic acid was boiled for 2 h, diluted with 20 ml ether at 20°C, and the precipitate was filtered and washed with ether. After recrystallization from nitromethane, 0.94 g (62%) of II was obtained, identical to that described in [1].

4-Bromo-6,8-dimethyl-9-cyano-4a,10a-cis-4,4a-trans-1,2,3,4,4a,10a-hexahydrobenzothiazolo[3,2-a]pyridinium Perchlorate (V). A mixture of 0.56 g (1 mmole) of I and 3 ml of 70% perchloric acid in 12 ml acetic acid was heated for 10 min at 80-90°C. The reaction mixture was cooled to 20°C, diluted with 20 ml ether and the precipitate filtered. After recrystallization from nitromethane, 0.33 g (78%) of V was obtained, identical to that in [1].

Analogously, the perchlorates V and VI were obtained from II and III with yields of 83 and 85%, respectively (Table 1).

4-Bromo-6,8-dimethyl-9-cyano-4a,10a-cis-4,4a-trans-1,2,3,4,4a,10a-hexahydrobenzothiazolo[3,2-a]pyridinium 1,1,3,3-Tetracyanopropenide (VIII). A mixture of 2 mmole III or V and 0.36 g (2 mmole) VIII in 10 ml methanol was stirred at 25-40°C for 30 min. The precipitate was filtered and recrystallized from nitromethane. The yield of VIII was 89 and 83%, respectively (Table 1).

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