5,13,14H-Benzo[d,e]isoquinolino[2',3'-a]quinazoline-5,13-dione (VI). A mixture of 0.4 g (2 mmole) of anhydride IIIa and 0.42 g (3.2 mmole) of anthranilic acid amide was triturated until a homogeneous mass was obtained, and the mass was then heated to 240°C and maintained at this temperature for 1.5 h. The mixture was dissolved in the minimum amount of chloroform and chromatographed with a column (silica gel 100/250, chloroform) with collection of the fraction containing a substance with yellow luminescence (R_f 0.6). The solvent was removed by distillation to give 0.15 g of VI.

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CONFORMATION OF 4,5,6-SUBSTITUTED 2-ISOPROPYL-1,3,2-OXATHIOBORINANES

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The configuration and predominant conformations of 2-isopropyl-4,5,6-alkylsubstituted 1,3,2-oxathioborinanes have been studied by ^{1}H-NMR spectroscopy. 2,4- and 2,6-Dialkylsubstituted derivatives exist in near half-chair conformations, while 6,6-dimethyl-2-isopropyl-1,3,2-oxathioborinane exists in two energetically equivalent inverting forms. 2,5,6- and 2,4,6-Trialkylsubstituted 1,3,2-oxathioborinanes consist of mixtures of stereoisomers differing in the orientations of the alkyl groups at the $C_{(6)}$ and $C_{(4)}$ ring atoms.

2-Isopropyl-5-alkylsubstituted 1,3,2-oxathioborinane molecules exist predominantly in half-chair conformations [1]. The present paper deals with an examination of the conformations of 2-isopropyl-1,3,2-oxathioborinanes (I-VI), containing alkyl substituents in the 4,5, and 6-ring positions.

Analysis of the signal multiplicities in the ^{1}H-NMR spectra (Table 1) of compounds I and II reveals that they exist primarily in chair-like conformations with an equatorial methyl group at the $C_{(4)}$ and $C_{(6)}$ atoms, respectively. A distinguishing feature of the spectrum of compound II relative to that of compound I are the lower values of the vicinal spin-spin coupling constants (SSCC) $^3J_{H_AH_a}$ and $^3J_{H_CH_a}$. This is apparently due to the fact that introduction of a methyl group in the 6-position of the 1,3,2-oxathioborinane ring results in greater distortion of the ring than does introduction of the same group at the $C_{(4)}$ atom.

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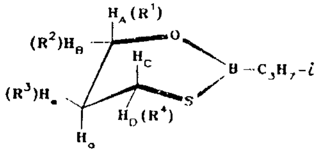
TABLE 1. ^{1}H-NMR Spectral Parameters of Alkyl-substituted 1,3,2-Oxathioborinanes



Compound						Chemical shifts, δ, ppm						SSCC, Hz							
№	R^1	R^2	R^3	R^4	isomer	H_A	H_B	H_C	H_D	H_a	H_e	$^3J_{Aa}$	$^3J_{Ba}$	$^3J_{Ae}$	$^3J_{Be}$	$^3J_{Ca}$	$^3J_{Da}$	$^3J_{Ce}$	$^3J_{De}$
I	H	H	H	CH_3	—	3,93	4,17	2,99	—	1,58	2,00	9,9	3,6	2,6	4,6	9,8	—	3,8	—
II	H	CH_3	H	H	—	4,07	—	2,6		1,59	2,02	8,8	—	2,4	—	8,8	5.8	4,6	4,6
III	CH_3	CH_3	H	H	—	—	—	2,61		1,77		—	—	—	—		6,2,	3,4	
IV	CH_3	H	CH_3	H	cis	—	4,12	2,35	2,63	2,0	—	—	2.7	—	—	9,0	4.3	—	—
	H	CH_3	CH_3	H	trans	3,78	—	2,41	2,59		—	7,2	—	—	—	8,2	3,8	—	—
V	CH_3	H	*i*-C_3H_7	H	cis	—	4,22	2,35	2,63	1,3	—	—	3,3	—	—	12,3	4,0	—	—
	H	CH_3	*i*-C_3H_7	H	trans	4,20	—	2,50	2,71		—	12,2	—	—	—	6,5	3,9	—	—
VI*	H	CH_3	H	CH_3	cis	4,01	—	3,0		1,74	1,98	10,5	—	1,6	—	10,5	—	3,4	—
	H	CH_3	H	CH_3	trans	4,30	—	3,0		1,68	1,77	7,5	—	4,5	—	—	3,3	—	6.3

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*In the cis-isomer the R^4 substituent occupies the position of the equatorial hydrogen atom H_D, in the trans-isomer that of the axial atom H_C.

The dihedral angles between the spin-coupled protons were estimated based on their corresponding SSCC values, using a modified Karplus equation taking into account substituent electronegativity [2] (Table 2); these estimates suggest that the half-chair conformations in compounds I and II are somewhat flattened, just as in the series of 2,5-dialkylsubstituted 1,3,2-oxathioborinanes [1]. As can be seen from Table 2, the distortions of the corresponding angles are greater at the thioether side of the molecule than at the ether side.

The same conclusion is reached based on comparison of their ^{13}C-NMR spectral data. The resonance signals for atoms $C_{(4)}$, $C_{(5)}$, and $C_{(6)}$ are observed at 22.54, 33.43, and 69.72 ppm, respectively, in the spectrum of compound I, and at 32.24, 36.02, and 64.03 ppm for compound II. The significant difference in the chemical shifts of the $C_{(4)}$ atoms in the two compounds is consistent with our conclusion that there is greater distortion of the chair-like molecular conformation of compound II.

Replacement of both hydrogens attached to atom $C_{(6)}$ (compound III) produces an equilibrium condition between two inverting, energetically equivalent forms. This is indicated by the magnetic equivalence of the methyl groups attached to $C_{(6)}$ and the triplet structure of the methylene group proton signals for the $C_{(4)}$ and $C_{(5)}$ atoms.

An alternative proposition, namely, that compound III exists predominantly in a twist-boat conformation, is excluded based on the observation that in the ^{1}H-NMR spectrum the resonance signals due to the methylene and methyl group protons are broadened as the temperature is lowered, due to retardation or suppression of the inversion process.

Another feature of the ^{1}H-NMR spectrum of compound III is the anisotropy of the protons in the enantiotopic methyl groups within the isopropyl substituent attached to the boron atom; these protons appear in the form of two doublets with $\Delta\delta = 0.12$ ppm. The enantiotopic methylene group protons attached to the $C_{(4,5)}$ atoms are isotropic, but anisogamous, which is clear from the narrow fine splitting of the central components in their triplet resonance signals.

Compound IV exists as a mixture of stereoisomers, as evidenced by the doubling of the resonance signals for individual group protons and ^{13}C nuclei, as well as by the presence of complex multiplets resulting from signal overlap of nuclei with similar chemical shift values. For instance, the resonance signals for the methyl group protons attached to $C_{(5)}$ and $C_{(6)}$ consist of four doublets at 0.95, 1.01, 1.16, and 1.28 ppm. The predominance of a chair-like conformation for the ring stereoisomers is confirmed by the observed vicinal SSCC values for the ring protons and by their magnetic nonequivalence (Table 1).

The configuration of these stereoisomers was determined based on analysis of the SSCC values for the protons attached to the $C_{(4-6)}$ atoms in the ring. As can be seen from the data in Table 1, the values of these parameters indicate a diequatorial orientation of the methyl groups at $C_{(5,6)}$ in one of the isomers and an axial-equatorial orientation in the second isomer. According to general principles of conformational analysis for saturated six-membered ring 1,3-heterocyclic systems, including 1,3,2-dioxaborinanes [3-5], the trans-isomer featuring a diequatorial orientation of methyl groups should be energetically more favorable. An alternative conformation for the trans-isomer, with a diaxial orientation of methyl groups, is distinguished based on its relatively high nonbonded interaction energies for the synaxial substituents (9.2-10.0 kJ/mole), and can therefore be excluded from consideration.

In the case of the cis-isomer with an axial-equatorial orientation of methyl groups, two conformers are possible, having a 5a,6e- or 5e,6a-arrangement of substituents. It is known [1], however, that in the series of 2,5-dialkyl-1,3,2-oxathioborinanes, as well as in the series of 2,5-dialkyl-1,3,2-dioxaborinanes [5], the conformer with an axial alkyl group attached to the ring $C_{(5)}$ atom is not in fact observed. This is supported by the greater conformational energy for an axial alkyl group attached to the $C_{(5)}$ atom in this series compared to in the series of 2,5-substituted 1,3-oxathianes (2.9-3.1 kJ/mole [6]). On the other hand, however, the conformational energy for an axial methyl group attached to $C_{(6)}$ in a substituted 1,3-oxathiane has been estimated as 4.1-6.2 kJ/mole [6], and includes the nonbonded synaxial interaction energy with the protons attached to the $C_{(2)}$ and $C_{(4)}$ ring atoms. If one assumes that in the case of the cis-isomer of compound IV only one such interaction is present, namely, $CH_3(C_{(6)})$—$H(C_{(4)})$, then the axial orientation of the methyl group attached to $C_{(6)}$ in the cis-isomer should be energetically favored over the equatorial orientation.

The axial orientation of the methyl group attached to $C_{(6)}$ is deduced as well from the values of the vicinal SSCC for the proton attached to the same atom with the $C_{(5)}$ protons

TABLE 2. Calculated Dihedral Angles Values between Vicinal Protons

Compound	Isomer	Dihedral angles, φ_{HH}(°)					
		A*a*	B*a*	A*e*	C*a*	D*a*	C*e*
I*	—	198	61	68	205	—	57
II**	—	200	—	70	215	46	52
IV	cis	—	49	—	213	52	—
	trans	207	—	—	217	55	—
V	cis	—	45	—	190	53	—
	trans	172	—	—	225	54	—
VI	cis	187	—	58	203	—	56
	trans***	209	—	39	—	56	—

* $\varphi_{H_BH_e}=56°$.

** $\varphi_{H_DH_e}=50°$.

*** $\varphi_{H_DH_e}=40°$.

(Table 1). It must also be noted, however, that the values of $^3J_{H_CH_a}$ and $^3J_{H_AH_a}$ are somewhat lower than expected for a half-chair conformation, in which the heteroatom fragment in the ring is planar; this is due to the distortion of the ring.

Furthermore, as can be seen from the results in Table 2, the dihedral angle values in compound IV differ substantially from those for a classical chair conformation. This distortion leads to additional weakening of the nonbonded interactions between the axial methyl group attached to $C_{(6)}$ and the axial protons attached to $C_{(4)}$.

The ^{1}H-NMR spectrum of 2,5-diisopropyl-6-methyl-1,3,2-oxathioborinane (V) is on the whole similar to the spectrum of compound IV, suggesting the presence in the sample of two stereoisomers with 5e,6e- and 5e,6a-substituent orientations. The ring conformation in this case, however, is more folded compared to compound IV (cf. Table 1 and the corresponding dihedral angle values given in Table 2).

Compound VI also consists of a mixture of stereoisomers. Based on analysis of the multiplet for the $C_{(4)}$ proton, however, the methyl group attached to this atom in the trans-isomer occupies an axial position. No spectral indications of ring inversion were observed for this stereoisomer.

The conformational behavior of 2,4,5,6-substituted 1,3,2-oxathioborinane molecules differs significantly from the properties of substituted 1,3-dioxanes, 1,3-dithianes, and 1,3-oxathianes; the distinction lies in the fact that in the case of 1,3,2-oxathioborinanes an axial orientation of a substituent attached to the $C_{(5)}$ atom is energetically unfavorable. This is apparently a consequence of stronger or greater nonbonded 1,3-interactions between an alkyl group and the unshared electron pairs on the heteroatoms in the 1,3,2-oxathioborinane ring. The ring conformation in the latter is therefore influenced to a much larger extent than in 1,3-dioxanes or 1,3-oxathianes by the degree of substitution of the $C_{(4)}$, $C_{(5)}$, and $C_{(6)}$ atoms, due to the absence in 1,3,2-oxathioborinanes of 1,3-nonbonded interactions between the synaxial substituents attached to the $C_{(2)}$ atom, which stabilize the ring conformation of 1,3-dioxanes and 1,3-oxathianes.

EXPERIMENTAL

^{1}H- and ^{13}C-NMR spectra were recorded on Tesla BS-497 (100 MHz) and Bruker AM-250 (250 MHz) spectrometers using 10 and 50% solutions in tetrachloromethane and C_6D_6, versus TMS as internal standard.

Dihedral angle values between vicinal protons were estimated based on the equality of calculated, using the equation in [2], and experimental SSCC values. The program for carrying out these calculations was written in BASIC for an Élektronika DZ-28 microcomputer.

Compounds I, II, and VI were synthesized according to [7]. 1,3,2-Oxathioborinanes III, IV, and V were prepared in an analogous manner by reaction of the corresponding substituted 3-mercaptoalkan-1-ols [8] and isopropyldichloroborane [9].

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EFFECT OF STRUCTURAL FACTORS ON THE BASICITIES AND ELECTRONIC SPECTRA OF BETAINE ALDEHYDES OF AZOLES AND YLIDS OF MALONIC ESTER AND DIMEDONE

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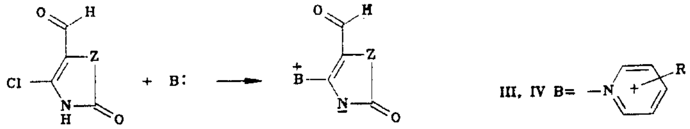
Betaine aldehydes of thiazole and imidazole containing substituted pyridinium and isoquinolinium cations were synthesized and their basicities were determined. The effect of the type of charge separation (betaine and ylid) and the nature of the heteroatoms and substituents in the onium and anionoid parts of the molecules on their electronic spectra and basicities was studied; the principles established are presented in the form of linear dependences.

Important data regarding the electron interactions in compounds with structures of the inner organic salt type [1] are obtained by a study of their basicities; of the two modifications of structures with separated charges — betaines and ylids [2, 3] — the basicities of the former have been studied to a considerably smaller extent.

To fill this gap and to compare the properties of ylids and betaines we, in addition to the already described betaines IIIa, k and IVa [4, 5], accomplished the synthesis and determined the basicities of new betaine aldehydes IIIb-j of thiazole and thoroughly analyzed the literature data on the basicities and electronic spectra of ylids V and VI of malonic ester [6] and dimedone [2, 7, 8]. Betaines IIIa-k were obtained by previously developed methods [4, 5] starting from the corresponding chloroformylazolinones I and II [9] and substituted pyridines and isoquinolines.



I, II IIIa-k IVa

I, III Z=S; II, IV Z=N—Ph; III, IV a R=H, b R=3-CH_3, c R=3-C_2H_5, d R=3-*i*-C_3H_7, e R=3-$CH_2C_6H_5$, f R=4-CH_3, g R=4-C_2H_5, h R=4-*i*-C_3H_7, i R=3,4-$(CH_3)_2$; j R=4-COC_6H_5, k R=3,4-phenylene

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