APPLICATION OF NMR SPECTROSCOPY TO THE STUDY OF THE THREE-DIMENSIONAL STRUCTURES OF HYDROGENATED HETEROCYCLES (REVIEW).

II.* CONFIGURATIONS AND CONFORMATIONS OF THE HETERORINGS

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The results of determinations of the configurations and conformations of heterorings containing N, O, Si, P, S, Ge, As, Sn, Se, Sb, and Te atoms by ^1H, ^{13}C, ^{15}N, ^{19}F, and ^{13}P NMR spectroscopy are correlated. Publications that are of interest from a methodical point of view are primarily summarized in the review.

The number of publications devoted to investigations of the configurations and conformations of heterorings by NMR spectroscopy presently exceed 6000 communications, according to estimates that are far from complete. As in the preceding part of this review [1], those studies that most clearly illustrate the general approach from a methodical point of view are discussed here. A fragmentary list of some of the publications pertaining to the theme of this review has been presented in a two-volume monograph [2, 3].

Three-Membered Heterorings

In this case there are no conformational problems with respect to the form of the ring; however, in the case of aziridines, for example, invertomers that are stable at ordinary temperatures develop because of impeded inversion of the pyramid of nitrogen bonds [4, 5]. The configurational problems are solved on the basis of the $^3J_{HH'}$ and $^2J_{NCH}$ spin-spin coupling constants (SSCC) and δ_H and δ_C chemical shifts. It is apparent from Table 1 that $^2J_{HH'}{}^{cis} > {}^3J_{HH'}{}^{trans}$ in all cases; this may serve as an analytical sign of the configuration relative to the C_2 and C_3 atoms and is in qualitative agreement with the Karplus dependence for the $^3J_{HH'}$ constant [see [1], formulas (1) and (2)]. In the case of aziridines (X = N) the spatial orientation of the N-alkyl group has a distinct effect on $^3J_{HH'}{}^{cis}$ (see [1], p. 1597) and on the chemical shifts of the syn and anti ring protons. The N-tert-butyl group gives rise to deshielding of the syn proton due to an induced dispersion interaction, while other alkyl substituents, on the other hand, give rise to greater shielding of this proton due to the diamagnetic anisotropy of the N—C bond [11]. This shielding decreases in the order N—Me > N—Et > N—iso-Pr.

The magnitude of the $^2J_{^{14}NCH}$ constant in the spectra of aziridines depends on the orientation of the unshared electron pair (UEP) of the nitrogen atom [12]. The $^2J_{^{15}NCH}$ constants are discussed in [13], in which it is shown that the $^2J_{^{15}NH}$ constant is greater [from (—) 3.6 to (—) 4.6 Hz] in the case of a syn orientation of the orbital of the UEP of the nitrogen atom relative to the C—H bond under consideration than in the case of an anti orientation [∿(—) 1 Hz]. The latter depends markedly on the nature of the solvent.

The changes in the NMR parameters in other aziridines [14-17] and oxiranes [18-21] have been described in the indicated studies. The stereochemical effects of pyridine as a solvent are discussed in [19]. Some cases of the shielding effects from three-membered rings [22, 23] and the ^{13}C NMR spectra [15, 24] have been examined.

The cis-trans-configurational isomerization and the barrier to inversion of nitrogen in 2,3-diphenyl-3-methyloxaziridine (E_a = 97.1 kJ-mole^{-1}) have been studied by NMR spectroscopy [25]. The barrier to inversion of nitrogen in 2-methyl-3,3-disubstituted oxaziridines

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*See [1] for Part I.

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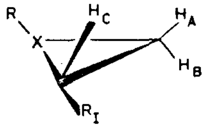
TABLE 1. Geminal $^2J_{HH'}$ and Vicinal Spin-Spin Coupling Constants (SSCC) and Average Values of the δ_H and δ_C Shifts in Three-Membered Rings



SSCC	Atom X, substituents, and SSCC (in Hz)			
	X = CH_2, R_1= various substituents [6]	X=N [7]	X=O, R_1=Ph, CN, COMe, COOH [8]	X=S, R_1=Me [9]
$^2J_{AB}$	from −3,1 to 13,0	from +3,0 (R=$SiEt_3$) to −6,8 (R=F)	+5,8±0,5	⩽0,4
$^3J_{AC}$	4,3—14,5	4,5 (R=$SiEt_3$) 8,0 (R=Cl)	4,6±0,5	6,3
$^3J_{BC}$	1,2—10,2	3,1±0,2 (5,6±0,2 when R=Cl, Br)	2,2±0,5	5,4
δ_H, ppm*	0,22	1,62	2,54	2,27
δ_C, ppm†	−3,5	28,5	39,5	18,7

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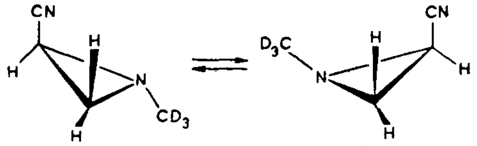
*For unsubstituted rings, the δ_H chemical shifts vary over a wide range, depending on the character and amount of substitution (for example, from 5.5 to 0.2 ppm when X = CH_2 [6]).

†The carbon-13 shifts for unsubstituted rings are indicated; the shift for N-methylaziridine is presented for X = N [10]; the signals are reckoned from tetramethylsilane.

is ∿ 58.6 kJ-mole^{-1} higher than in 1-methyl-2,2-dimethylaziridines. The barrier to inversion of nitrogen in the aziridine ring has been calculated by the MO self-consistent-field (SCF) CNDO/2 method in connection with an interpretation of the NMR data [26]. A thorough experimental determination of the equilibrium ($\Delta H°$ and $\Delta S°$) and activation ($\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$) parameters in the case of N-trideuteromethyl-2-cyanoaziridine (Ia ⇄ Ib) was made in [5].



Ia Ib

Replacement of one of the CH_2 groups in aziridine by NH leads to an increase in the barrier to inversion of the nitrogen atom. In the case of 1,3-dimethyl-2-benzyl-3-benzyldiaziridine at −10°C one of the invertomers with trans-oriented oribitals of the unshared electron pairs (UEP) of two nitrogen atoms (from NMR data) can be crystallized out from the diastereoisomeric mixture (1:1).

Four-Membered Heterorings

The most accurate data on the three-dimensional structures of four-membered heterorings are obtained from an analysis of the spectra in the microwave and far-UV regions [28]. Commencing in 1970, the conformations of four-membered heterorings began to be studied by ^1H NMR spectroscopy. The stereospecificity of the vicinal $^3J_{HH'}$ constants is most often used as the principal structural criterion [29-31], the long-range $^4J_{HH'}$ and $^4J_{HNCCH'}$ constants are sometimes used [32, 33], while the stereospecifity of the proton shielding constants is seldom used [31]. It has been established for azetidines, oxetanes, and thietanes that the protons of the axial methyl groups and the vicinal trans-axial protons are characterized by larger $^3J_{HH'}$ constants than the corresponding equatorial protons.

The height of the barrier to inversion and deviation angle α for four-membered heterorings as compared with cyclobutane are presented in Table 2. It can be seen that in the

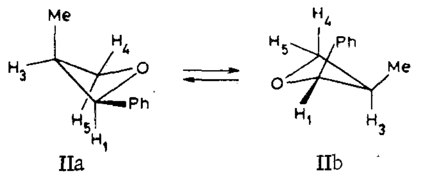
TABLE 2. Height of the Barrier to Inversion and Deviation Angle α for Four-Membered Heterorings and Cyclobutane [34]

Molecule	Barrier	α, deg	Data from NMR and other methods
	kJ · mole⁻¹		
Oxetane [35,36]	0,18	5	Calculation of $\Delta\sigma$ [31, 37], ^{1}H NMR of the stereoisomers [38]
Thietane [39]	3,3	28—40	^{1}H NMR parameters [40, 41]
Azetidine [42]	5,3	15—20	^{1}H NMR data [43]
Cyclobutane [28]	5,4 6,2	23—25	Ab initio calculation [44], shielding effects [45]

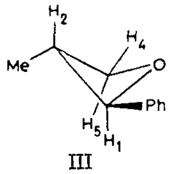
TABLE 3. R Factors in Oxetanes [46]

J^{trans}/J^{cis}	R factor			
	cis-II	trans-II	Oxetane	2-Phenyloxetane
J_{12}/J_{13}	—	—	0,76	0,94
J_{25}/J_{24}	—	0,90	0,76	0,85
J_{34}/J_{35}	0,77	—	0,76	0,69
J_{34}/J_{24}	—	—	0,76	0,61
J_{25}/J_{35}	—	—	0,76	0,95

case of oxetane (X = 0) the heteroring is evidently almost planar. However, an analysis of the δ_H and $^3J_{HH'}$ parameters of the ^{1}H NMR spectra of diastereoisomeric 2-phenyl-3-methyloxetanes obtained by stereospecific synthesis [46] shows that trans-oxetane III resides primarily in the dipseudoequatorial saddle conformation, while the cis-oxetane (IIa ⇄ Ib) exists primarily in the form of an equilibrium mixture (1:1) of two saddle conformations. This can also be judged from the values of the R factors (see [1], p. 1591) presented in Table 3, which was composed on the basis of the data on $^3J_{HH'}$ summarized in Table 4. In the case of oxetane, in which a rapid inversion of the "saddle"—"saddle" type undoubtedly occurs, R = 0.76. In cis-oxetane II, R = J_{34}/J_{35} = 0.77, i.e., it is approximately the same as in oxetane, whereas R = J_{25}/J_{24} = 0.90 in trans-oxetane III. It may therefore be asserted that cis-oxetane II is a mixture of conformers in a ratio of 1:1.



IIa IIb



III

According to the R-factor method, $\cos^2\psi = 3/(2 + 4R)$, where ψ is the angle of rotation of one CH_2 group relative to the other about the C—C bond. Consequently, for oxetane when R = 0.76, we find that $\alpha \sim 33°$ (α = the deviation angle of the ring) from the expression $\tan(\alpha/2) = 2\sqrt{2}\tan\psi$ (see 1, p. 1590, ψ =), which contradicts the data in Tables 2 and 4. The R-factor method as applied to four-membered heterorings can evidently be regarded only as a method for the rough estimation of α. The application of the DAERM method [47] is fraught with a number of arbitrary assumptions with respect to the Karplus coefficients $J_{HH'}^{\circ}$ and bond angles γ in the Newman projection (angle ω, Fig. 1).

The conformations of four-membered heterorings can be determined more accurately from the ratio of the trans-vicinal constants $b^2 = {}^3J_{aa}/{}^3J_{ee}$ [see [1], formula (7)] with allowance for the orientation of the unshared electron pair of heteroatom X [48], while the $^3J_{HH'}$ constants themselves indicate the configuration of the substituents. The α angle has a value on the order of 30-37° in 3-chlorothietane, which exists in the preferred saddle conformation with a pseudoequatorial orientation of the chlorine atom, according to data on the dipole moments and the Kerr constants [41]. The use of the method of the ratio of the trans constants leads to smaller angles (Table 4). Angle α is 15° in 2-phenylazetidine [43]. X-ray diffraction analysis [49, 50] of crystalline samples of other azetidines leads to α values of 11-14°.

TABLE 4. Spin-Spin Coupling Constants (Hz) of the Protons in Four-Membered Heterorings and Ring Deviation Angles (the Atoms Are Designated in Accordance with Formulas II and III, R Designates the Substituent Attached to the Nitrogen Atom)

Compound					$^3J_{12}$ trans	$^3J_{13}$ cis	$^2J_{23}$ gem	$^3J_{24}$ trans	$^3J_{25}$ trans	$^3J_{34}$ cis	$^3J_{35}$ gem	$^2J_{45}$ gem	$^4J_{14}$	$^4J_{15}$	α, deg
X	R	R¹	R²	R³											
O	—	H	H	H	6,60	8,70	—	8,70	6,60	6,60	8,70	—	0,14	0,20	0
O	—	Ph	H	H	7,31	7,79	−10,91	9,15	7,74	5,62	8,19	−5,75	−0,02*	−0,03*	5
O	—	Me	H	H	6,86	7,43	−10,77	8,93	7,77	5,61	8,30	−5,79	−0,20	−0,40	5
O	—	Ph	Me	H	—	8,10	(7,10)†	—	—	5,66	7,33	−5,59	0,0	0,0	
O	—	Ph	H	Me	6,67	—	(6,80)†	8,10	7,28	—	—	−5,60	0,0	0,0	
S	—	Me	H	H	7,7	7,9	−11,7	9,1	8,2	5,2	7,9	−8,7			8
S	—	Ph	H	H	9,2	7,8		9,6	9,2	3,1	8,1				18
N	H	Ph	H	H	8,4	8,0	−10,6	8,5	9,4	3,5	7,8	−6,6	−0,80	−0,40	15
N	Cl	Ph	H	H	9,4	8,5	−10,1	7,7	10,3	2,4	8,6	−7,1	−1,30	−1,10	21
N	Cl	Me	H	H	9,3	8,3	−10,0	7,6	10,8	2,7	8,4	−7,2	−1,30	−0,80	20

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*Value of −0.26 and −0.35 Hz, respectively, are presented in [43] for these constants.

†The vicinal $^3J_{CH_3H}$ constants are indicated in parentheses.

The cis and trans isomers of 2,2,3,4,4-pentamethyl-1-oxophosphetane have been identified by ^{1}H NMR spectroscopy by means of the Eu(dpm)3 shift reagent [51]. A large shift of the proton attached to C_3 in the cis isomer is observed in this case, and this indicates coordination of europium with the phosphoryl oxygen atom.

Fluorine-19 NMR spectroscopy has been used to study the conformatin of perfluoro-2-halo-1,2-oxazetidines [52]. The difference in the conformational free energies was estimated at 3.8-4.2 kJ-mole^{-1}. Stereoisomeric azetidin-2-ones have been studied by ^{1}H NMR spectroscopy [53].

The following characteristic peculiarities of the NMR parameters in four-membered heterorings can be cited: 1) in the case of a pseudoequatorial orientation of 3-CH_3 its signal is split into a doublet by the methylidyne proton with a smaller constant than in the case of a pseudoaxial conformation, 2) the pseudoaxial 3-H proton in oxetanes resonates at greater field than the pseudoequatorial proton, while the 4-H protons display inversion of the shielding constants [37, 54, 55]; these experimental facts are in complete agreement with the expected changes in the shielding constants estimated from the magnetic-anisotropic effects in accordance with dipole and nondipole approximations [37]; 3) the geminal constants in oxetane ($^2J_{45}$ = −5.79, and $^2J_{23}$ = −10.77 Hz) are in agreement with the concept that their algebraic value increases as the s character of the carbon atom increases. From the formula $^1J_{CH} = 500\ a_H^2$ for oxetane we find that $a_H^2 = 0.296$ for the C_2 and C_4 atoms and 0.275 for the C_3 atom, since the square of the hyperfine coupling constant (a_H^2) is a measure of the s character, we then see agreement with the observed tendency of the change in $^2J_{HH'}$.

Five-Membered Heterorings

The interpretation of the ^{1}H NMR data in five-membered heterorings from the point of view of their three-dimensional structures is the most complicated case. Here the conformation is determined not only by the steric 1,2 interaction in the ring but also by the steric interaction of the substituents, in this case the 1,3 interactions are weakened as compared with the analogous interactions in six-membered rings. Nonplanar conformations of the "half-chair" (HC) and "envelope" (E) type with angular strain prove to be more advantageous due to a decrease in the energies of the eclipsed 1,2 interactions (the Pitzer strain in cyclopentane is ∿ 16.7 kJ-mole^{-1}).

The five-membered heteroring usually exists in a state of rapid pseudorotation between all of the possible HC and E forms. As demonstrated in Fig. 2 and below, the conformation of the five-membered ring in the pseudorotation cycle can be described by torsion angle φ_j and pseudorotation phase angle Δ [56, 57]

$$\varphi_j = \varphi_m \cos(0.5\Delta + j\delta), \qquad (1)$$

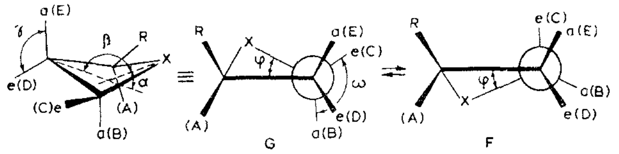
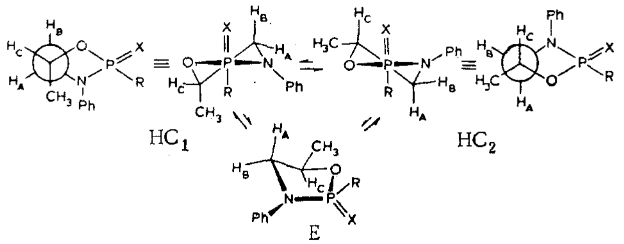


Fig. 1. Determination of the angles in four-membered heterorings: α) deviation angle, β) saddle angle; γ) bond angle; φ) torsion angle; ω) bond angle in the Newman projection.

where j = 1, 2, 3, and 4, $\delta = 144°$, and φ_m is the maximally possible torsion angle, which in cyclopentane is 48° (form C_2) and 46° (form C_s). The introduction of heteroatoms in the ring and substituents leads to a decrease in the symmetry, an increase in the number of different conformers, and, possibly, to greater energic advantageousness of some one conformation. However, the latter does not mean "freezing" of the pseudorotation but only indicates the apparent (on the NMR time scale) existence of the heterorings in the HC or E conformation (either a distorted half chair or a twisted envelope, depending on the statistical weights of the HC and E conformations).

In the case of five-membered heterorings a complete analysis of the SSCC requires allowance for the electron orbitals (EO) and the orientation of the heteroatoms (see [1] , p. 1596). As an example, let us examine the ^{1}H NMR and ^{1}H-{^{31}P} nuclear magnetic double resonance spectra of cis-N-phenyl-2-oxo-2-phenoxy-5-methyl-1,3,2-oxazaphospholidine (IV), which are presented in Fig. 3. This example is convenient in that the conclusions drawn on the basis of the dependence $^3J_{HH'} = f(\theta,\lambda_i^\varphi)$ [see [1], Eqs. (15) and (16)] can be confirmed by the dependence $^3J_{PXCH} = F(\theta)$. In the case of cis isomer IV a change in the temperature from + 30 to −70°C does not lead to a substantial change in the $^3J_{HH'}$ and $^3J_{PH}$ constants, whereas they do change in the case of the trans isomer. This fact and the large difference in the $^3J_{PA} = 2.0$ and $^3J_{PB} = 15.2$ Hz constants in the case of cis isomer IV (in the case of the trans isomer these constants are $^3J_{PA} = 6.3$ and $^3J_{PB} = 8.9$ Hz and change with the temperature) make it possible to assume that the molecules of the latter exist primarily in half-chair conformation HC_2 in the pseudorotation cycle (Scheme 1).

Scheme 1



Cyclic torsion angle ψ = 55°, which considerably exceeds the ψ angles found for other five-membered heterorings [60] was found in [58, 59] on the basis of $^3J_{HH} = f(\theta)$ but without allowance for the orientation effect of the heteroatoms for similar compounds [$R = N(CH_3)_2$, X = O]. An estimate of ψ with allowance for the effect of orientation of the heteroatom on the $^3J_{HH'}$ constant in five-membered heterorings can be made only by the method of successive approximation.

a) A zero approximation (an empirical approach without allowance for the EO of the heteroatoms) can be obtained by the R-factor method. For example, for cis-N-phenyl-2-oxo-2-methylthio-5-methyl-1,3,2-oxazaphospholidine (V) we have $^3J_{aa} = {}^3J_{AC} = 9.0$ Hz, and $^3J_{ae} = {}^3J_{BC} = 6.0$ Hz, the missing constants can be taken from [59]: $^3J_{ee} = {}^3J_{DB} = 3.1$, and $^3J_{ea} = {}^3J_{DA} = 7.5$ Hz, and then R = 0.89, and torsion angle ψ = 43°, i.e., it is substantially less than 55°.

b) A first approximation (an empirical approach with allowance for the EO of the heteroatoms) can be obtained by the Forrest method (see [1], pp. 1594-1595). We will use morpholine, in which the $N{-}CH_2{-}CH_2{-}O$ fragment is similar to the carbon part of V, to determine

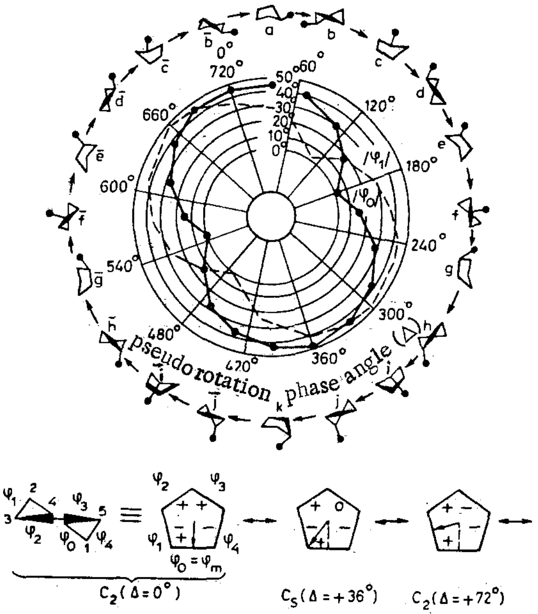


Fig. 2. Topological diagram of the pseudorotation of methylcyclopentane and determination of the torsion (φ_j) and phase (Δ) angles.

the $J_{HH'}{}^{\circ}$ constant. From the formula $\cos\psi = [({}^3J_{HH}{}^{exp} + 0.3)[J^\circ]^{1/2}$ by substituting ${}^3J_{ae}$ = ${}^3J_{BC}$ = 6.0 Hz, we then estimate torsion angle ψ = 38°, which is somewhat less than in the case of the estimate in the zero approximation.

c) The second approximation (an empirical approach) takes into account the EO and the orientation of the heteroatoms and is carried out by an iteration procedure guided initially by ψ = 38° and using expressions (15) and (16) presented in part I of the review [1]. Using the experimental value ${}^3J_{BC}{}^{exp}$ = 6.0 Hz and assuming ΔE_o = 1.30, ΔE_N = 0.85, and ΔE_C = 0.40, we find that ψ = 30°, which is in good agreement with the other data and extended Hückel method MO LCAO calculations of the ${}^3J_{HH'}$ constants in V (see [1], literature cited No. 67). The vicinal ${}^3J_{HH'}$ constants in V (see [1], literature cited No. 67). The vicinal ${}^3J_{PA}$ = 2.0 and ${}^3J_{PB}$ = 15.2 Hz constants confirm the half-chair HC_2 form with ψ = 30°.

Stable half-chair conformations are sometimes realized in bicyclic compounds. For example, this is the case in the VI Cation [61] (Fig. 4). Here the ${}^3J_{46}$ = 12.0 and ${}^3J_{35}$ = 11.5 Hz constants leave no doubt as to the correctness of the conformation of both rings depicted in Fig. 4, since such high values of the vicinal constants undoubtedly can be observed only for dihedral angles θ ∿ 180°.

Derivatives of Tetrahydrofuran (THF) and Thiophenes. The ${}^3J_{HH'}$ constants found by a complete analysis of the ${}^1H$ NMR spectra of cis- and trans-2,5-dimethoxytetrahydrofuran [62] (an AA'BB'XX' spin system) from the LAOCOON-3 program show that the molecules of the compounds most likely do not exist in the "envelope" or "half-chair" form but rather in intermediate forms. The specific increments in the chemical shifts of the 3-CH_3 protons in 2-aryl-5-hydroxy-3-methyltetrahydrofurans have been analyzed thoroughly [63]. The conformation of furan and thiophene aldehydes [64] with respect to the stereospecificity of the ${}^5J_{HH'}$ constant have been examined. The configurations and conformations of γ-lactones (50 compounds) with respect to proton–proton SSCC were analyzed thoroughly in [65].

Nitrogen-Containing Heterocycles. 4-Oxoprolines, cis- and trans-4-substituted prolines [66], and N-substituted pyrrolidones [67] have been investigated by ${}^1H$ NMR spectroscopy, however, researchers were unable to draw any conclusions regarding their conformations. All of the SSCC were derived by analysis of the proton spectra (100 and 220 MHz) of 3-azabicyclo[3.1.0]hexane (VII) and its derivatives [68]. In this case the five-membered fragment can have an envelope conformation or a planar form. The ${}^2J_{44}$ = ${}^2J_{22}$ = −11.6 + 0.2 Hz and ${}^3J_{HH'}$ constants indicate a chair conformation for the entire bicyclic system. The inversion of the

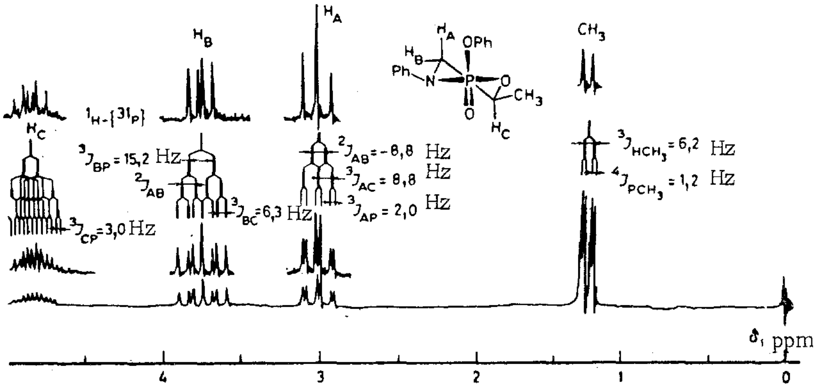
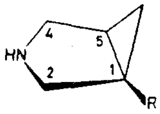
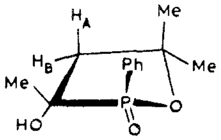


Fig. 3. ^{1}H and ^{1}H-{^{31}P}nuclear magnetic double resonance spectra of cis-N-phenyl-2-oxo-2-phenoxy-5-methyl-1,3,2-oxazaphospholidine (IV) at +20°C for a 5% solution in CHC_{13} and ν_0 = 100 MHz.

endocyclic nitrogen atom as a function of the temperature and the character of the substituents attached to the nitrogen atom was discussed by means of the NMR method in the case of five-membered rings with two nitrogen atoms, viz., 2- and 3-pyrazolines, pyrazolidine, and pyrazolidone [69], while the effects of the anisotropy of the magnetic susceptibility in them were examined in [70]. The effects of an asymmetric endocyclic nitrogen atom in pyrazolidines have been discussed on the basis of the chemical shifts of the methyl protons [71]. The ^{1}H NMR spectra of stereoisomeric isoxazolidines have been examined [72],



VII



VIII

while in [73] and subsequent publications of this series the conformational equilibrium is discussed with respect to the vicinal $J_{HH'}$ and J_{PH} constants in similar compounds with phosphorus-containing substituents.

Phospholenes and Oxophospholenes. Compounds of this type have been examined by ^{1}H NMR spectroscopy [74-78]. Unfortunately, the conformation of the rings in them has not been discussed, although this problem is of paramount importance from a methodical point of view, since the spectra of these compounds contain information regarding the geminal $^2J_{^{31}PCH}$ constants and their dependence on the orientation of the unshared electron pairs (UEP) of phosphorus and the P═O bond. The ^{1}H NMR spectrum of 3-hydroxy-2-oxo-2-phenyl-3,5,5-trimethyl-1,2-oxaphospholane (VIII) was discussed in [78], and from the $^3J_{PCCH}$ constants, which are of the same order for H_A and H_B, and the δ_H shifts it was concluded that this compound has an envelope conformation with an oxygen atom at the apex of the flap. The conformations of the cis and trans stereoisomers of similar compounds in which a diethylamino grouping is attached to the phosphorus atom instead of a phenyl group have been studied in detail by means of ^{1}H NMR spectroscopy and the IR spectra [79]. Other forms have been established in the crystalline state [80].

1,3-Diheterorings. Systems of this sort have been studied more thoroughly, since in these cases the ring protons form either typical AA'BB' or simpler spin systems. In the case of 1,3-dioxolanes because of the fact that the C—O bond is shorter than the C—C bond, one can approximately assume the C_2 form with a minimal energy at a torsion angle (φ_m in the $O—CH_2—CH_2—O$ fragment of ∿ 40°. According to the x-ray diffraction data for 1,3-didioxolanyl (IX), the OCH_2CH_2O fragment is not maximally twisted, and the torsion angle is no greater than 30°. The torsion angles calculated from Eq. (1) and found by experimental methods are presented in Table 5 [81]. Thus the Δ = 19.1° and φ_m = 30.3° values found indicate that the conformation of 1,3-didioxolanyl (IX) is intermediate between C_2 (Δ = 0°) and C_s (Δ = 36°) (X).

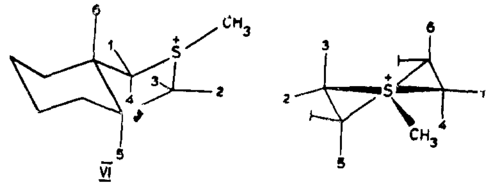
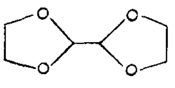


Fig. 4. Conformation of the trans-3-methyl-3-thioniabicyclo[4.3.0] nonane cation (VI) from the vicinal $^3J_{16} = 6.5$, $^3J_{46} = 12.0$, $^3J_{25} = 6.0$, and $^3J_{35} = 11.5$ Hz constants.

TABLE 5. Calculated and Experimentally Established Torsion Angles in Crystalline 1,3-Didioxolanyl (IX)

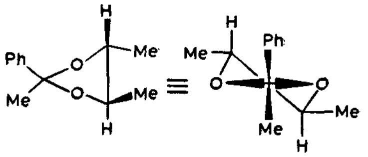
Angles	Calculated		Exptl., $\Delta + 19.1°$
	C_2 (Δ=0°)	C_s (Δ=36°)	
φ_0 (φ_5-1)	+30,3°	+29,1°	+30,3°
φ_1 (φ_1-2)	−24,8	−29,1	−27,9
φ_2 (φ_2-3)	+9,5	+18,0	+13,6
φ_3 (φ_3-4)	+9,5	0	+4,6
φ_4 (φ_4-5)	−24,8	−18,0	−20,7



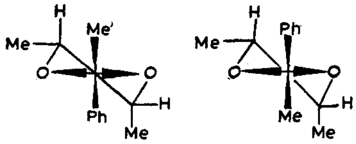
IX

X

The ^{1}H NMR spectra of stereoisomeric 1,3-dioxolanes XI-XIII (Tables 6) have been analyzed rather fully.* It is apparent from Table 6 that the methylidyne and methyl groups attached to C_4 and C_5 in XI form an X_3ABY_3 spin system, whereas in the case of XII and XIII they form an $X_3AA'X'_3$ spin system. In the case of the virtual dipseudoequatorial conformer of trans isomer XI trans constant $^3J_{AA'} = {}^3J_{AB} = 8.3$ Hz, we demonstrated above in the case of oxazaphospholidine IV that this value of the constant is typical for the case in which the equilibrium is shifted to favor a half-chair conformation for XI. The $^3J_{AA'}$ cis constants of 5.40-6.45 Hz for the cis-4,5-dimethyl isomers (XII and XIII) indicate a significant contribution of other conformations.



XI



XII

XIII

pseudorotation

The effects of the anisotropy of the magnetic susceptibility of the substituents attached to the C_2 and C_4 atoms were discussed qualitatively in [82]. It was shown that the γ-syn-methyl group gives rise to a −0.15 ppm shift (to lower field) of the proton signal, whereas a γ-syn-phenyl group leads to a +0.17 ppm shift. The ^{1}H NMR spectra (300 MHz) of cis- and trans-2-trifluoromethyl-4-substituted and 2,2-bis(trifluoromethyl)-1,3-dioxolanes have been examined by subspectral analysis [83]. It was concluded that a virtual unsymmetrical half-chair conformation with an axial CF_3 group is preferred in the case of the trans isomers, whereas an unsymmetrical half-chair conformation with a dipseudoequatorial orientation of the substituents is preferred in the case of the cis isomers. The conforma-

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*The initial assignment of the configuration was later corrected [83]; data with allowance for this correction are presented in the present review.

TABLE 6. δ_H Chemical Shifts and $^{3}J_{HH'}$ SSCC in the Spectra of 1,3-Dioxolanes

Compound	Sample form	δ_H, ppm			SSCC, Hz		
		CH_3 (4,5)	CH_2 (2)	CH	^{3}J AA′	^{3}J AX	^{4}J AX′
XI (trans-4,5)	10% in CCl_4	1,23 1,11	1,57	4,67 4,35	8,30	5,95	0,0
XII (cis -2,4)	10% in CCl_4	1,12	1,55	3,91	6,45	6,44	−0,23
XIII (trans-2,4)	10% in CCl_4	0,99	1,48	4,24	5,40	6,46	−0,21
cis-2,2,4,5-Tetramethyl-	100%	1,05	—	4,15	5,85	6,30	−0,25
trans-2,2,4,5-Tetramethyl-	100%	1,15	—	3,38	8,35	6,90	−0,15

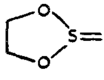
tions of 2-substituted (CH_3, iso-C_3H_7, and C_6H_5) 1,3-dioxolanes and 1,3-dithiolanes have been examined [84, 85]. The ring protons here form an AA'BB' system, all of the $^{2}J_{HH'}$ and $^{3}J_{HH'}$ constants and δ_H shifts were found, and the presence of pseudorotation with, however, the preferred existence of pseudoequatorial conformations was demonstrated. A comparison of 1,3-dioxolane ring is included as a structural fragment, were examined in [85, 88-90]; however, the conformations of the five-membered ring were not discussed in detail because of the complexity of the spectra.

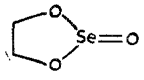
The dipole-dipole interaction constants ($D_{HH'}$) have been studied by analysis of the ^{1}H NMR spectrum of 2,2-dimethyl(d_6)-1,3-dioxolane dissolved in nematic p-(p-ethoxybenzoxy)-phenyl butyl carbonate [91]. It was concluded that the spectrum in the nematic phase does not improve our knowledge of the geometry of 1,3-dioxolane molecules.

It has been shown that in the spectra of 4,5-cyclano-1,3-dioxolanes the $^{2}J_{HH'}$ constants for the 2-CH_2 group are positive, while the $^{4}J_{HH'}$ constants (0-0.5 Hz) do not belong to the "W" form and change in an unpredictable fashion [92]. The δ_H shifts of cis- and trans-2,4-di- and 2,4,4-trisubstituted 1,3-dioxolanes have been presented [93, 94]. However, these data must be used with allowance for the footnote presented above. The ^{1}H NMR spectra (300 MHz) of cis- and trans-2-methyl-4-halomethyl-1,3-dioxolanes have been studied in connection with their conformation [95]. Stereoisomeric 2,2-dimethyl-4,5-disubstituted 1,3-dioxolanes, the additive increments of the δ_H shifts of the 2-CH_3 groups, and the ring conformation were discussed in detail in [86].

The principal ^{1}H NMR parameters and their peculiarities in the spectra of stereoisomeric 1,3-oxathiolanes [96-98] and 1,3-oxathiolan-5-ones [99] have been examined. The existence of a flexible conformation of the five-membered heteroring was demonstrated, and in the case of 2,5-disubstituted oxathiolanes attention to the C_s conformation with an oxygen atom at the apex of the flap of the "envelope" was stressed [97]. On the other hand, an equilibrium of the "envelope ⇄ envelope" form [100] with the C_5 atom at the apex of the flap was proposed in the case of 4-methyl-1,3-oxathiolanes.

1,2,3-Triheterorings. The conformations of ethylene sulfite (1,3,2-dioxathiolane 2-oxide) (XIV), cis- and trans-4-methyl-, cis- and trans-4,5-dimethyl-,* and gem-dimethyl-substituted ethylene sulfites have been studied [101-105]. On the basis of the $J_{HH'}$ constants it was concluded qualitatively that an envelope conformation with a pseudoaxial S=O bond is realized in all cases. It was established that the S=O bond has a deshielding effect on the syn protons and the syn methyl groups in the 4 and 5 positions. A similar conclusion was previously drawn [104] on the basis of quantitative estimates of the effects of anisotropy of the magnetic susceptibility of the S=O and S-O bonds.


XIV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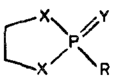
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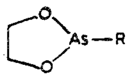
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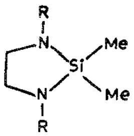
XVIII

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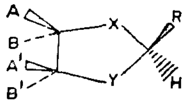
*The configurational isomers here are due to the rigidity of the pyramid of the bonds of the O_2S=O grouping.

TABLE 7. Chemical Shifts and SSCC in the Spectra of Five-Membered Heterorings



Compound			δ_H, ppm				KCCB, Hz		
X	Y	R	H_A	$H_{A'}$	H_B	$H_{B'}$	$^2J_{HH'}$	$^3J_{HH'}^{cis}$	$^3J_{HH'}^{trans}$
S	S	Me [85]	3,25		3,15		−11,32	5,49	6,62
S	S	Ph [85]	3,42		3,27		−11,25	5,21	6,55
O	O	Me [85]	3,96		3,88		−7,68	7,20*	6,06*
O	O	Ph [85]					−7,26	7,16	6,19
O	S†	Et [87]	4,26	2,94	3,71	2,94	−9,28 (O) −10,06 (S)	5,44 ($J_{AA'}$) 4,37 ($J_{BB'}$)	4,01 ($J_{AB'}$) 10,36 ($J_{BA'}$)
O	S‡	Ph [87]	3,96	2,73	3,39	2,56	−8,59 (O) −9,31 (S)	6,72 ($J_{AA'}$) 6,51 ($J_{BB'}$)	2,79 ($J_{AB'}$) 8,39 ($J_{BA'}$)

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*These constants are $^3J_{HH'}{}^{cis}$ = 6.15 Hz and $^3J_{HH'}{}^{trans}$ = 7.10 Hz in the spectra of cis- and trans-2,2-dimethyl-4,5-diisopropyl-1,3-dioxolanes XIV, in which the cis and trans orientations of the coupling protons is proved absolutely unequivocally by the nonequivalence (cis isomer) and equivalence (trans isomer) of the 2-CH_3 groups [86]. We are evidently dealing with the apparent orientation here, since in all of the compounds in this table the molecules exist in the pseudorotation state, whereas in the case of the trans isomer of XIV the equilibrium should be shifted to favor the dipseudoequatorial conformation.

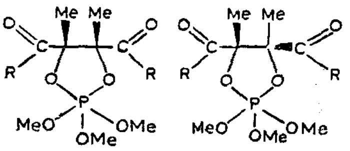
†These data pertain to solutions in CCl_4.

‡For solutions in benzene.

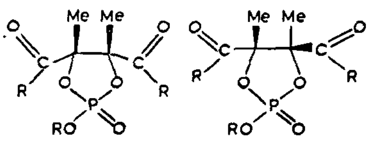
The ^1H NMR spectrum of 1,3-dioxa-2-selenone (XV) and the spectrum of XIV indicate nonplanarity of the ring and an axial orientation of the Se=O bond [102].

The ^1H and ^{31}P NMR spectra of the meso and dl isomers of hydroxyphosphoranes (XIX) and 1,3,2-dioxaphospholanes (XX) were examined in [106-108].

It was shown that the chemical bonds of pentacovalent phosphorus in XIX exist in a state of rapid permutational isomerization (Berry pseudorotation of the trigonal bipyramid or tourniquet rotation of the square pyramid [109]) and that the chemical shifts of all the proton-containing grups in the diastereomers of XIX and XX have characteristic differences; in the dl form of XX the methyl groups (including R = CH_3) display nonequivalence, and the resonance of the ^{31}P nuclei of the meso form of phosphorane XIX appears at higher field than in the case of the dl form ($\delta_{^{31}P} \sim -50 \pm 2$ ppm). The conformation of the heteroring was not discussed. A brief communication regarding oxaphosphoranes that, in our opinion, contains important results has been published [110].



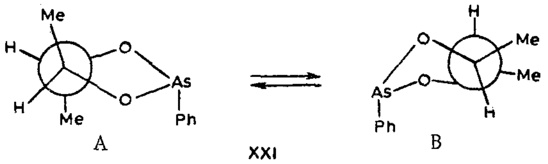
meso XIX dl



meso XX dl

The ^1H and ^{31}P NMR parameters in the spectra of phosphineimines XVI (X = NCH_3, Y = NZ, and R = H) [111] and diazophospholanes [X = NCH_3, Y = O, R = Oph, Cl, $N(CH_3)_2$] [112] have been presented. The ring conformation is discussed qualitatively in the latter communication.

The ^1H NMR spectra of cis- and trans-4,5-dimethyl-1,3,2-dioxarsolanes XVII (R = Cl and Ph) [113], the configurations and conformations of 1,3,2-dioxa-, 1,3,2-oxathia-, and 1,3,2-dithiaarsolanes [114], and polyhedral stereoisomerism and pseudorotation in arsapyran systems [115] have been examined. Since the pyramid of bonds of the arsenic atom is characterized by a barrier to inversion of ∿ 105-176 kJ-mole^{-1}, at ordinary temperature cis isomer XVII can exist in syn and anti forms, which can be interconverted via inversion of the arsenic atom; however, only one form was found from the NMR spectrum, while the anti and syn forms are present in a ratio of 5:1 in the case of cis-4,5-dimethylethylene sulfite XIV. The $^3J_{HH'}$ constants in the spectra of XVII are discussed in [113] on the basis of the conformational equilibrium between the two twist and envelope XXIA and XXIB forms with a pseudoaxial phenyl group.



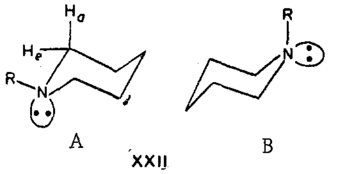
XXI

The conformations of silicon-containing five-membered rings with nitrogen [XVIII, R = $Si(CH_3)_3$] and oxygen atoms in the 1,3 positions have been examined by ^1H NMR spectroscopy [116, 117]. The singlet character of the line of the ring protons indicates planarity of the ring and trigonal hybridization of the nitrogen atom, the p orbital of the unshared electron pair of which is evidently included in d conjugation with the silicon orbitals.

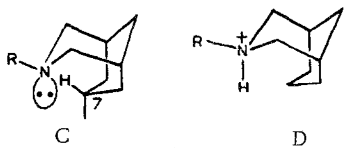
Six-Membered Heterorings

Six-membered heterorings are classical subjects for NMR studies. This is due to the fact that the lifetimes of the molecules in forms that are close to canonical systems (chair, boat, and twist) are relatively long in six-membered rings and to the fact that the stereospecificity of any SSCC and chemical shifts is displayed most prominently in this case.

Nitrogen-Containing Rings. Among the compounds of this type, piperidine and diazines all by themselves and as structural fragments of more complex compounds are of particular interest. The parameters of the ^1H NMR spectra of piperidine (XXII) and 3-azabicyclo[3.3.1]-nonane (XXIII) were described completely for the first time in [118, 119], however, according to [120], the orientation of substituent R attached to the nitrogen atom in them has been interpreted incorrectly. The geminal $^2J_{HH'}$ constant of the methylene



XXII

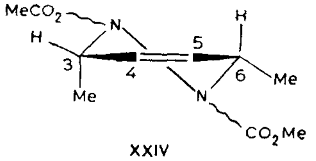


XXIII

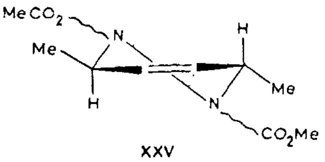
group adjacent to the nitrogen atom provides additional argumentation regarding the position of R (see [1], p. 1602). In the spectrum of 1-methyl-3,3,5,5-d_4-piperidine this constant was found to be −11.2 Hz at −83° [119], which constitutes evidence in favor of the A conformation for XXII (see [1], Scheme 2). Data from the dipole-moment method confirm this conclusion [121]. The C conformation, in which the endo proton in the 7 position experiences pronounced deshielding under the influence of the anisotropy of the magnetic susceptibility of the axial unshared electron pair, is realized in XXIII. The nonequivalence ($\Delta\delta_{ae} = \delta_e - \delta_a$) of the protons of the adjacent methylene group may serve as an additional indication of the orientation of the substituent attached to the nitrogen atom in N-alkylpiperidines. If R is isotropic (for example, as in the case of a methyl group), it should have a slight effect on $\Delta\delta_{ea}$ in the case of an equatorial orientation that is symmetrical with respect to both hydrogen atoms.

The chemical equilibrium associated with inversion of the pyramid of bonds of the nitrogen atom in protonated cis-2,6-dimethylpiperidine and cis-3,5-dimethylmorpholine was examined by ^{1}H NMR spectroscopy [122]. The ^{1}H NMR parameters of stereoisomeric 1,2,5-trimethyl-4-phenylpiperidin-4-ols have been discussed [123]. A significant contribution of the distorted boat conformation with a boat-equatorial orientation of the phenyl group was demonstrated.

The conformations of the ring in cis- and trans-1,2-bis(methoxy-carbonyl)-3,6-dimethyltetrahydropyridazines (XXIV and XXV) and 1,2-bis(ethoxycarbonyl)- and 1,2-bis(trifluoroethoxycarbonyl)-1,2,3,6-tetrahydropyridazines have been examined by ^{1}H and ^{19}F NMR spectroscopy [124, 125]. The half-chair conformation in XXIV undergoes rapid interconversion only at 140°C, whereas at −5°C inversion of the nitrogen atoms is slowed down to such an extent that nonequivalence of the ester groups develops in the ^{1}H NMR spectrum. In the spectrum of cis isomer XXIV at room temperature the 3- and 6-CH_3 groups, as well as the 3- and 6-H and the 4- and 5-H protons, are nonequivalent in pairs and are characterized by $^3J_{34}$ = 4.0, $^3J_{56}$ = 1.4, and $^3J_{45}$ = 9.2 Hz. In the case of the XXIV conformation dihedral angles θ_{34} and θ_{56} should be $\sim$ 40 and 80°, respectively, according to the Karplus dependence (with allowance for sp^2 hybridization of one of the carbon atoms), the observed $^3J_{HH'}$ constants actually correspond to them.

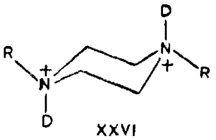


XXIV



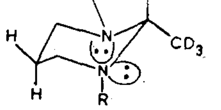
XXV

Interconversion of the ring of 1,2-dimethylhexahydropyridazines has been studied by ^{13}C NMR spectroscopy [126]. The advantageousness of the diequatorial orientation of the N–CH_3 groups was demonstrated. The inversion of the nitrogen atoms and interconversion of the ring of 1,4-dimethylpiperazinium dications (XXVI) has been investigated extremely thoroughly [127].



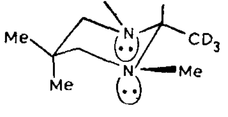
XXVI

The peculiarities of the ^{1}H NMR parameters in substituted 1,3-diazines (XXVII and XXVIII) are of particular interest in the study of the stereochemistry of nitrogen-containing rings. The so-called "rabbit-ear effect" [128, 129], which consists in repulsion of the 1,3-syn-diaxial orbitals of the unshared electron pairs of the two nitrogen atoms (XXIX) and is a special case of the more general "anomeric effect" [130, 131], is manifested in this case. The same effect regulates the preferred conformation of 1,2,4,5-tetramethyl-1,2,4,5-tetrazine (XXX) [132], which is realized at −87°C. The N–CH_3 groups display two lines (2.85 and 3.52 ppm, coalescence temperature −35°C) under these conditions, while the CH_2 groups display an AB quartet ($^2J_{ae}$ = −11.6 Hz, coalescence temperature −24°C).



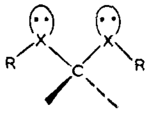
δ_{H_a} 2.81 ppm (R = Me)

XXVII



δ_{H_a}=2.21 ppm

XXVIII



XXIX

The $\Delta G^{\neq}$ parameters for inversion of the ring of N-alkyltetrahydro-1,3,5-thiadiazines (XXXI) and N-alkyldihydro-1,3,5-dithiaazines (XXXII) have been determined [133].

Of the stereochemical studies devoted to substituted tetrahydro-1,3-oxazines, publications [134-138] are of special methodical interest. In the first of them it is demonstrated that oxazine molecules exist in the preferred chair conformation, while quantitative

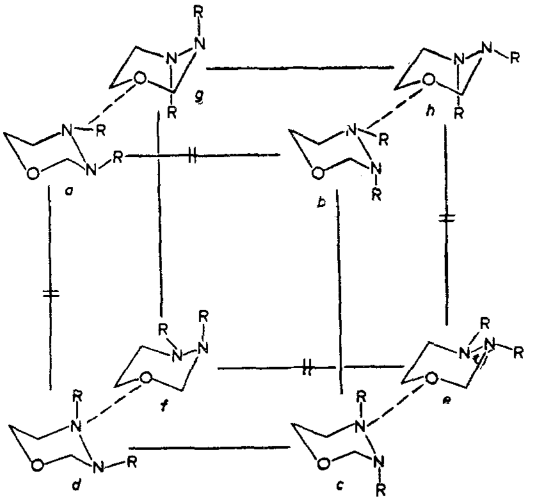
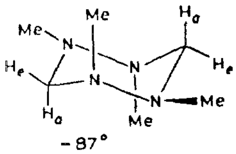


Fig. 5. Topological diagram of the conformational transitions of perhydro-1,3,4-oxadiazines [143].

estimates of the effects of anisotropy of the magnetic susceptibility and the effect of intramolecular electrical fields on δ for various conformations were made in the later publications. This required preliminary estimates of the effective anisotropies (χ): $\Delta\chi_{N-N} = 1.73 \cdot 10^{-6}$, $\Delta\chi_{C-N} = 2.01 \cdot 10^{-6}$, and $\Delta\chi_{\underline{N}} = 1.09 \cdot 10^{-6}$ cm^3-mole^{-1}(nondipole approximation); $\Delta\chi_{C-N} = 1.38 \cdot 10^{-6}$, and $\Delta\chi_{N} = 5.22 \cdot 10^{-6}$ cm^3-mole^{-1} (dipole approximation). Correlations with respect to δ_H have been made [136, 138]. The conformations and configurations of perhydrobenz-3,1-oxazines (XXXIII) have been studied on the basis of these correlations [139].



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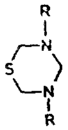
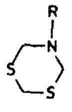


XXXI



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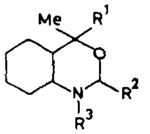
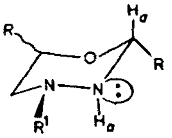
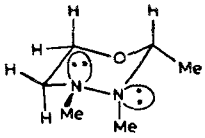


XXXIII



XXXIV



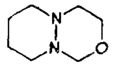
XXXV

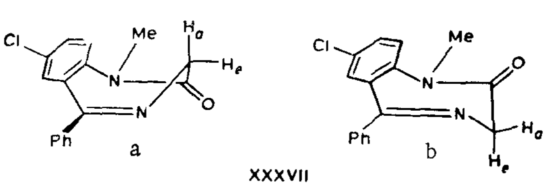
Substituted perhydro-1,3,4-oxadiazines (XXXIV and XXXV), in which two processes, viz., ring interconversion and inversion of the pyramid of bonds of the nitrogen atoms, can exist, have been studied [140-143]. The topologies of both conformational processes are depicted in Fig. 5. The ^{1}H NMR spectrum of 3,4-dimethyltetrahydro-1,3,4-oxadiazine at 34°C indicates the rapid rates of the two processes. As the temperature is lowered, "eclipsed ring inversion" (which proceeds through a conformation with eclipsed exocyclic bonds of the nitrogen atom) is slowed down initially, but the other inversion pathways are retained. At −30°C the methylene group in the 2 position displays an AB quartet with $^2J_{ae} = -10.5$ Hz, which indicates slowing down of "free ring inversion" with $\Delta G^{\neq}_c = 53$ kJ-mole^{-1}. New lines of the N−CH$_3$ groups of diequatorial conformer a appear as the temperature is lowered further (−77°C), and this indicates a decrease in the rate of "free inversion of the nitrogen atom" with $\Delta G^{\neq} = 52.0$ kJ-mole^{-1}. Measurement of the integral intensities of the lines at −80°C gives equilibrium constant $K = 0.22$ with form a as the minor component and, consequently $\Delta G^{\circ}_{153°K} = 1.9$ kJ-mole^{-1}. Conformer b is the principal form.

The introduction of a substituent in the 2 position leads to the realization in XXXIV and XXXV of the preferred chair conformation.

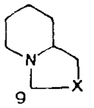
The conformational analysis of tetrahydro-2,5-dimethyl-1,2,5- and 2,4-dimethyl-1,2,4-oxadiazines by ^{1}H and ^{13}C NMR spectroscopy was carried out simultaneously and independently in [144, 145].

The conformational isomerization of 2-oxa-9,10-diazadecaline (XXXVI) [146] and 1,4-benzodiazepinones (XXXVII), which are effective minor tranquilizers, has been examined [147-149]. It is assumed that in the case of XXXVII the temperature dependence of the spectrum of the CH_aH_e group is due to inversion of the "boat—boat" type and that the preferred conformation at room temperature is boat form XXXVIIa [149]. However, the H_a proton in this conformation should experience the strong shielding effect of the aromatic ring, and under rapid interconversion conditions the resonance of the protons of the CH_2 group should, one would think, by no means be observed at ~ 4 ppm but rather at higher field. In our opinion, the absence of a contribution of chair form XXXVII requires additional quantitative substantiation by, for example, evaluation of the effects of the anisotropy of the magnetic susceptibility and the intramolecular electrical fields.

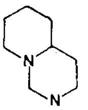

XXXVI



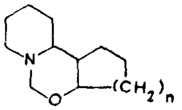
XXXVII



X = O,S,NR
XXXVIII



XXXIX



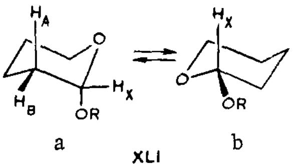
XL

The parameters of the ^{1}H NMR spectra and the configurations and conformations of 8-oxa-1-aza-, 8-thia-1-aza-, and 1,8-diazabicyclo[4.3.0]nonanes (XXXVIII) have been discussed qualitatively [150-153]. It was shown that the $^2J_{99'}$ constant is more positive in the trans-fused conformation, while $\Delta\delta_{99'}$ has a higher value (i.e., it is less negative) than in the case of cis fusion. The criterion of the effect of the mutual orientation of the unshared electron pairs of the nitrogen and oxygen atoms in the 1,3 positions on $^2J_{HH'}$ has been used to study the conformation of the fused rings of 1,3-diazabicyclo[4.4.0]-decanes (XXXIX) [154] and perhydrocycloalkano[e]pyrido[1,2-c][1,3]oxazines (XL) [155].

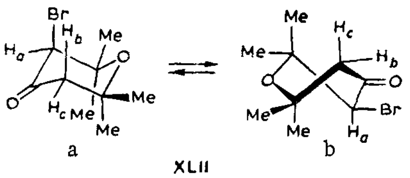
Oxygen-Containing Rings. The conformational equilibrium in 2-alkoxytetrahydropyrans (XLI) has been studied by means of the vicinal constants (an ABX system) [130, 156], it was concluded that the advantageousness of the axial form (the anomeric effect) is characterized by ΔG° = 0-4.2 kJ-mole^{-1}. It was found that there is a linear relationship between the square of the dipole moment (μ^2) and $J^{exp} = {}^3J_{AX} + {}^3J_{BX}$:

$$\mu^2 = 0.67 \cdot J^{\exp} - 2.25,$$

which makes it possible to predict μ from the J^{exp} value and, consequently, by comparison with μ^{calc} to determine the contribution of the alternative chair conformation and the conformation of the OR substituent.



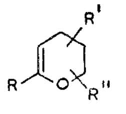
XLI



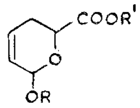
XLII

The ^{1}H NMR spectra of 5-bromo-, 3,5-dibromo, and 3,5,5-tribromo-2,2,6,6-tetramethyltetrahydropyran-4-ones (XLII) and the corresponding tetrahydropyranols have been described [157]. The high-field lines of the methylene AB quartet in the spectrum of the 5-bromo derivative were assigned to the equatorial H_c proton, since these lines display subsequent splitting under the influence of the H_a moment with long-range constant $|^4J_{ac}|$ = 1.0 Hz. The authors regard this as possible in the planar W-shaped fragment. The axial orientation of the bromine atom is considered to be proved by the presence of a bathochromic shift in the UV spectrum and the absence of a shift of the bands in the IR spectrum in the case of successive introduction of bromine in the α position relative to the C=O group. Unfortunately, other possible conformations such as the 1,4-twist conformation (XLIIb) were not discussed.

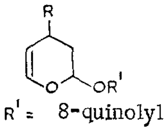
The preferred chair conformation was assigned to 3-ketolactose and β-D-galactose [158], acetonated α-L-sorbo- and β-D-fructopyranose [159], and β-L-erythro-pentapyranoside [169] on the basis of the $^3J_{HH'}$ constants, while cis and trans configurations and the chair form were assigned to 2,2-dimethyl-5-aminomethyl-4-oxotetrahydropyrans [161]. The conformations of a large number of substituted dihydropyrans XLIII have been discussed [162]. A 1,2-diplanar conformation was postulated for them. It has been established for esters of trans- and cis-2-alkoxy-5,6-dihydro-2H-pyran-6-carboxylic acids (XLIV) [163, 164] on the basis of the Karplus correlation for $^3J_{HH'}$ that the trans isomer exists in the preferred half-chair conformation with an equatorial ester group and a pseudoaxial alkoxy group, while the molecules of the cis isomer exist in conformational equilibrium.



XLIII



XLIV



XLV

The configurations and conformations of the cis and trans derivatives of 3,4-dihydropyran (XLV) have been examined on the basis of the ^{1}H NMR spectra [165]. The conformations were established from the $^3J_{HH'}$ constants and the long-range allyl $^4J_{HH'}$ constants (see [1], p. 1606), the trans isomers exist entirely in the half-chair conformation, whereas the cis-isomers are equilibrium mixtures of conformers in the "sofa" form.

The stereochemistry of cis- and trans-6-tert-butyloctahydrocoumarins, 10-methyl-1-oxa-cis-decalin, and cis-trans-1-oxa-2,3-decalones has been studied on the basis of the $^3J_{HH'}$ constants and the 10-CH_3 δ_H chemical shift [166, 167]. Chair and boat forms, which are rapidly interconverted at 60°C, are observed at 0°C in the spectrum of the 16-oxatricyclo-$[11.2.1.^{2,12}]$heptadec-14-en-17-one isomer with mp 85°C [168]. The anomeric effect in 2-substituted dihydropyrans and chromans has been studied by ^{1}H NMR spectroscopy [169].

The three-dimensional structures of 1,3-dioxanes have been investigated most completely by NMR spectroscopy. In this respect, more than 150 papers and several reviews have been published [170-172]. The orientation of the two oxygen atoms in the 1,3 positions creates conditions for the distinct separation of the resonance bands of the 2-CH_2, 4,6-CH_2, and 5-CH_2 grups in both the ^{1}H NMR and ^{13}C NMR spectra, in most cases this makes it possible to analyze the spectra within a first-order approximation. The principal conformation of 1,3-dioxane is the chair form, which was first demonstrated by the dipole-moment method [173, 174], after which it was confirmed by δH NMR spectroscopy [175, 176]. This fact was subsequently substantiated quantitatively by a determination of a difference in enthalpies ($\Delta H^\circ \approx$ 28 kJ-mole^{-1}) between the chair and twist forms from the heats of combustion [177].

The δ_H shifts in the spectra of 1,3-dioxane and analogous heterocycles for the preferred chair conformation are presented in Table 8. It is apparent that the protons attached to C_5 (as well as the methyl protons) experience inversion of the shielding constants. The reason for this phenomenon is explained by the effect of the anisotropy of the magnetic susceptibility of the orbitals of the unshared electron pairs of the two oxygen atoms [178].

The parameters of the ^{1}H NMR spectra of stereoisomeric 1,3-dioxanes and the effects of an aromatic solvent on them have been discussed [179-181]. Generalized and inverted anomeric effects in 2-substituted 4,6-dimethyl-1,3-dioxanes [182] and the conformational energies of the substituents in 5,5-disubstituted 1,3-dioxanes [183, 184] have been studied. The preferred chair conformation has been established for cis- and trans-2,5-disubstituted 1,3-dioxanes on the basis of vicinal $^3J_{HH'}$ constants [185]. The conformations of stereoisomeric 2,5-dialkyl-5-alkoxymethyl- [186], 2,5-dialkyl-5-(2-alkoxyethyl)- [187], and 2,5-dialkyl-5-(1-alkoxyethyl)-1,3-dioxanes [188] have been studied by comparison of the experimental nonequivalence of the $\Delta\delta_{AB}$ values of the methylene protons attached to the C_4 and C_6 atoms with the nonequivalence of the $\Delta\sigma_{AB}$ shielding constants estimated with allowance for the effects of anisotropy of the magnetic susceptibility and the intramolecular electrical fields for the canonical chair and unsymmetrical and symmetrical boat conformations. The configuration and conformations of 2-furyl-4,5,5-substituted and 4,5-dialkyl-1,3-dioxanes were studied in [190] and [191] respectively.

TABLE 8. δ_H Proton Chemical Shifts (ppm) in the Spectra of 1,3-Dioxane, 1,3-Dithiane, and Tetrahydro-1,3-oxazine in the Chair Conformation*

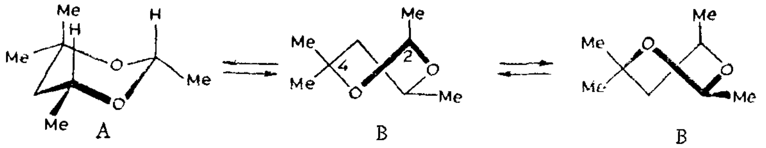
Spatial arrangement of the proton	1,3-Dioxane		1,3-Dithiane		Tetrahydro-N-methyl-1,3-oxazine	
2-H$_e$	4,87	ni	3,48	i	4,20	ni†
2-H$_a$	4,53		4,00		3,50	
4-H$_e$	4,00	ni	2,60	ni	2,70	ni
4-H$_a$	3,20		2,40		2,20	
5-H$_e$	1,24	i	2,09	ni	1,45	i
5-H$_a$	1,96		1,81		1,1	

---

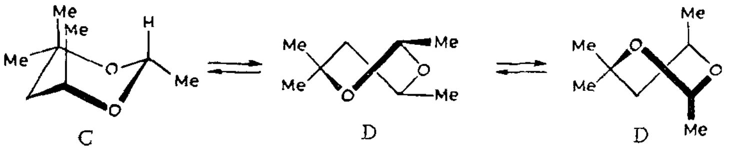
*The following abbreviations are used: ni indicates no inversion of the σ shielding constants, and i indicates that inversion of the σ constants does occur.

†The chemical shift of the 2-H protons depends markedly on the spatial orientation of the N-methyl group; the values presented correspond to an equatorial orientation.

It has been demonstrated by an analysis of the ^{1}H NMR spectra of cis- and trans-2,4,4,6-tetramethyl-1,3-dioxanes (XLVI) [192, 193] that the 1,3-syn-diaxial interaction of 4- and 6-CH$_3$ in the trans isomer shifts the conformational equilibrium markedly to favor the 1,4-twist conformation (D),



XLVI, cis isomer



XLVI, trans isomer

whereas in the cis isomer the 1,3-syn-diaxial interaction between the methyl group and the hydrogen atom (17.3 kJ-mole^{-1}) is not sufficient to invert the chair conformation (A) to the "flexible forms" (B).

In 2,2-disubstituted 4,4-dimethyl-1,3-dioxanes [194] the 1,3-syn-diaxial interaction between 2- and 4-CH$_3$ forces the molecule to assume a flexible form to an even more pronounced degree, however, when a 1-methyl-2-benzimidazolyl group is attached to the C$_2$ atom as a second substituent (XLVII), a 1,4-twist conformation [194], one of the signs of which is the $^3J_{ee'}$ constant of 3.1 Hz [it is on the order of $\sim$1.3 Hz in the chair conformation (see [1], p. 1598)], is primarily realized. However, a similar pattern is observed in the case of trans-2,2,4,6-tetramethyl-1,3-dioxane [177]. In the case of 2-alkyl-4,4-dimethyl-1,3-dioxanes, however, chair conformations with an equatorial alkyl group in the 2 position are preferred, according to ^{1}H and ^{13}C NMR spectroscopy. 2,2-Disubstittuted 4,6-dioxa-1,3-dioxanes have been studied by the same methods [195]. The three-dimensional structures of 2-alkyl-4,4,5-trimethyl- and 2-alkyl-4,4,6,6-tetramethyl-1,3-dioxanium perchlorates (XLVIII) are discussed in [196].

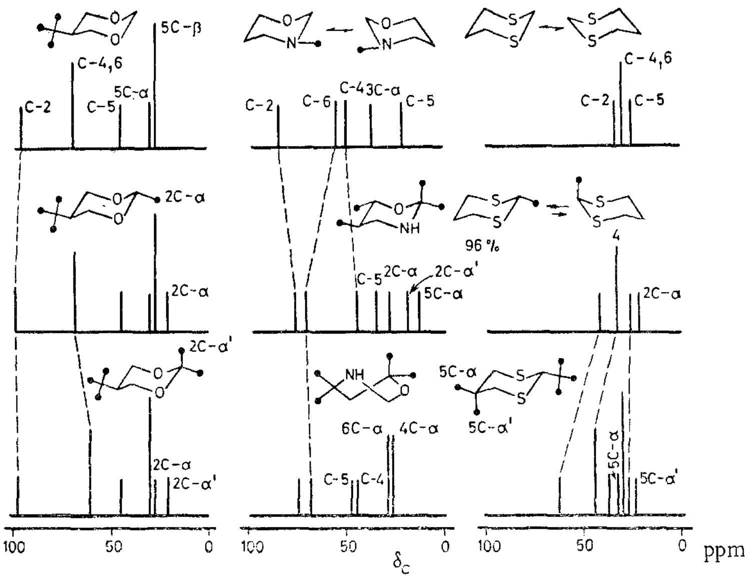
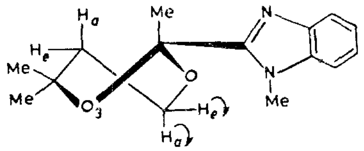
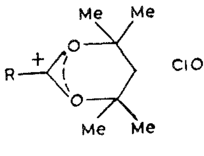


Fig. 6. Schematic picture of the ${}^{13}C$ NMR spectra of 1,3-dioxanes [206], tetrahydro-1,3-oxazines (author's data), and 1,3-dithianes [207].

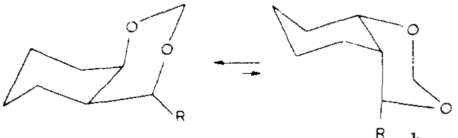


XLVII



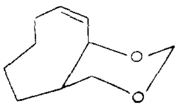
XLVIII

Polycyclic 1,3-dioxane derivatives have been studied. For example, it has been shown that for cis-1,3-dioxadecalane (XLIX) [197, 198] the advantageousness of the chair—chair form of the "O-inside" type (a) is 9.2 kJ-mole^{-1} as compared with the "C-inside" type (b), while cis-bicyclo[6.4.0]-10,12-dioxa-3-dodecene (L) exists primarily in the "O-outside" form [199], although in 1,3-dioxane itself a vinyl group as a substitutent in the 4 position has a greater A value ($-\Delta G^\circ = 0.001\ RT \ln K$) than an alkyl group in the 5 position.



a b

XLIX



L

A significant number of publications have been devoted to the orientation in the alkyl and aryl exo substituents themselves [200] attached to the C_2, C_4, and C_5 atoms. It was established from the ${}^3J_{HH'}$ constants that alkyl substituents prefer an anti-periplanar conformation relative to the C_4—C_5 bond, whereas the constants themselves are larger for axial than for equatorial substituents [201].

The conformational equilibrium in 5-fluoro-1,3-dioxane has been studied by ${}^1H$ and ${}^{19}F$ NMR spectroscopy [202] as a function of the properties of the solvent also in the case of dioxanes with spiro substituents attached to C_2 and C_5 [203, 205].

The peculiarities in the ${}^{13}C$ NMR spectra of 1,3-dioxanes [206] and their heteroanalogs [207] when ring interconversion is present and for the preferred conformations have been examined. Some of the spectra, from which the characteristics of the preferred conformations and a distinct difference in the δ_C shifts of the axial and equatorial C_α atoms are apparent, are presented schematically in Fig. 6. The increments of replacement by the δ_C shifts in

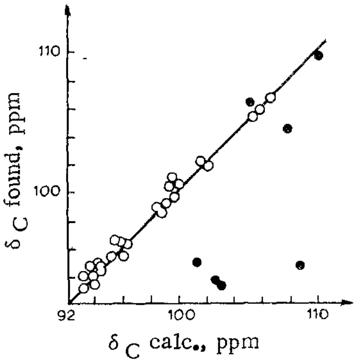
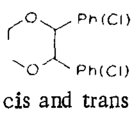


Fig. 7. Observed and calculated δ_C chemical shifts for the C_2 atom in 1,3-dioxanes, which exist in the preferred chair conformation. The data symbolized by ● correspond to cases with 2,4- and 4,6-syn-diaxial interactions in the chair conformation.

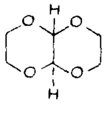
substituted 1,3-dioxanes, from which graphs similar to the graph in Fig. 7 can be constructed for each carbon, were isolated by means of an additive scheme. The calculated and observed δ_C shifts for, for example, the C_2 atom are in good agreement (with a correlation coefficient of 0.996) except for the compounds that exist in conformations other than the chair conformation (designated by black circles in Fig. 7).

1,4-Dioxanes. It has been established from the ^1H NMR spectra of cis- and trans-2,3-diphenyl- and 2,3-dichloro-1,4-dioxanes (LI) [208] recorded at room temperature and lower temperatures (down to −42°C) that the trans isomer of the former exists in a state of chair—chair inversion, while the trans isomer of the latter exists in the chair form, whereas the cis isomers exist in the state of a rigid boat form, since the protons of the $O{-}CH_2{-}CH_2{-}O$ grouping are nonequivalent. These assertions require, in our opinion, greater substantiation (the C_2 and C_3 atoms are chiral centers!). Torsion angles ψ have been examined by the R-factor method [209], while the effect of an aromatic solvent in 2-phenyl-1,4-dioxane, 1,4-oxathiane, 1,4-oxaselenane, and 1,4-dithiane was examined in [210]. A barrier to inversion of $\Delta G^{\neq} = 40.6$ kJ-mole^{-1} at −93.6°, which corresponds to a chair—twist process, was determined by a study of the temperature dependence of the ^1H NMR spectra of trans-2,3-trans-5,6-tetra-deutero-1,4-dioxane [211] and by examination of the ^{13}C satellites in 1,4-dioxane-d_7 [212, 213]. A rigid chair—chair conformation in trans-1,4,5,8-tetraoxadecalin (LII) [208] and cis fusion in tetraoxadecalins LIII [214] have been estabished. Anomalous long-range spin—spin coupling was detected in LIV [215]. The conformations of cis- and trans-2,3-dimethyl-1,4-dioxanes [216], the ^{13}C NMR spectra of stereoisomeric 1,4-dioxane-2,3-diols [217], and the parameters of activation of inversion of 3,3,6,6-tetramethyl-1,2,4,5-tetraoxane [218, 219] have been studied.

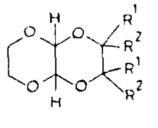


cis and trans

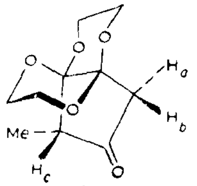
LI



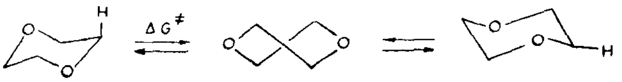
LII



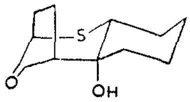
LIII

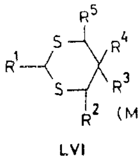


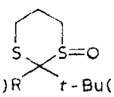
LIV

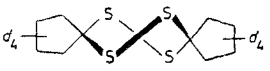


Sulfur-Containing Rings. The transannular interactions in 4-substituted thiacyclohexanes have been examined on the basis of the A values [200], and the γ effect and the stereochemistry of hydroxy-2-thiatricyclo[$7.3.1.0^{3,8}$]tridecanones LV have been examined [222] on the basis of the ^{13}C NMR spectra of cis-3,5-dimethylthiane [221]. A barrier to inversion of $\Delta G_{271}^{\neq} = 58$ kJ-mole^{-1} has been determined for 3,3,6,6-tetramethyl-1,2-dithiane [223]. The configurations and conformations, including the nonchair conformations, of substituted 1,3-dithianes LVI have been discussed in detail [224-235], and the equatorial conformation of the S=O bond in 1,3-dithiane 1-oxides LVII has been demonstrated [236]. The parameters of activation of chair—twist inversion have been found, and slow pseudorotation has been observed in the case of 3,3,6,6-bis(tetramethylene)-1,2,4,5-tetrathianes (LVIII) [238].

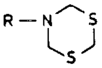

LV

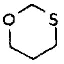

LVI

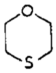

LVII

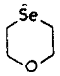

LVIII

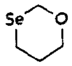
Nitrogen-, Oxygen-, Silicon-, Phosphorus-, Sulfur-, Arsenic-, Selenium-, Antimony-, and Tellurium-Containing Rings. The preferred conformations of N-alkylhydro-1,3,5-dithiazines (LIX) and N-alkyl-tetrahydro-1,3,5-thiadiazines [237], 1,3-oxathianes (LX) [238-244], 1,4-oxathianes (LXI) [210, 245] and their sulfoxides [246], 1,4-oxaselenanes (LXII) [210], and 1,3-oxaselenanes (LXIII) [247] have been studied and their $\Delta G^{\neq}$ values have been determined; the ^{13}C NMR spectra of stereoisomeric thianium salts have also been investigated [248].

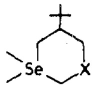

LIX

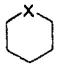

LX

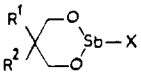

LXI


LXII


LXIII


LXIV

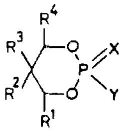
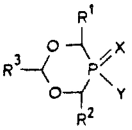

LXV


LXVI

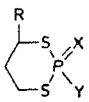
LXIV X=NMe,O,S,Se,Te,SiMe$_2$; LXV X=C,NR,O,S,Se,P^{III}, P^{V},As,Te
LXVI X=Cl,OMe,OEt

A preferred chair conformation (torsion angle ψ is greater than in cyclohexanes) in 3,3-dimethylsila-1-heterocyclohexanes and their derivatives (LXIV) [249] and a tendency for a change in the δ_C chemical shifts in the α, β, and γ positions in pentamethylene heterocycles LXV [250], the molecules of which exist in a state of rapid chair—chair inversion, have been established. The configurations and conformations of 1,3,2-dioxastibinanes (LXVI) have been studied [251]; rapid ring inversion, possibly without inversion of the pyramid of bonds of the antimony atom, occurs in the case of ring-unsubstituted stibinanes. A preferred chair conformation with an axial orientation of substituent X is realized in 4-methylstibines. Similar behavior of the ring has been established in 2,4,5-substituted 1,3,2-dioxaarsenanes [252], however, torsion angle ψ here (58°) is lower than in stibines (ψ = 61°).

More than 160 publications, many of which are correlated in earlier reviews [253, 254], have been devoted to studies of the three-dimensional structures of phosphorus-containing (P^{III} and P^{V}) heterorings by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The greatest attention has thus far been directed to 1,3,2-dioxaphosphorinanes LXVII [253, 255, 256]. The first



X=UEP,O,S ; Y,R$_i$ = var. sub.

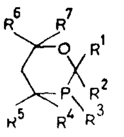
LXVII LXVIII


X=UEP,S ; Y= var. sub.

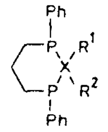
LXIX

UEP, unshared electron pair; var. sub., various substituents.

publications dealing with the conformations of 1,3,5-phosphorinanes LXVIII appeared recently [257], and some 1,3,2-diazaphosphorinanes [258] and 4-substituted 1,3,2-dithiaphosphorinanes LXIX [259] have been described. The conformations of stereoisomeric 1,3-oxaphosphorinanes LXX have been studied on the basis of the δ_C and δ_P chemical shifts and the $^1J_{PC}$, $^2J_{PCH}$, $^2J_{PCC}$, and $^3J_{PCCH}$ constants and by means of lanthanide shift reagents [260], while the barriers to interconversion have been determined on the basis ^1H and ^{31}P NMR spectra for 1,3-diphosphorinanes LXXI [261, 262], the barrier to inversion of phosphorus was found to be relatively low ($\Delta G_c^{\neq}$ ∼ 75-120 kJ-mole^{-1}). The dynamics of the permutational isomerization of many spiro heterocycles with pentacoordinated phosphorus [263, 264] and arsenic [265] atoms have been studied. Twist—boat forms have been established in some substituted 1,3,2-oxazaphosphorinanes [266, 267] and 1,3,2-dithiaphosphorinanes [268]. The ^1H NMR spectra of phosphorinane itself are very complex, but the α, β, and γ effects have been studied by ^{13}C NMR spectroscopy [249].

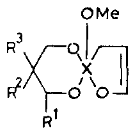


LXX



X = C,Si,Ge

LXXI

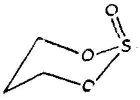


X = P,As

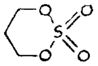
LXXII

The abundance and depth of the manifestations of the stereochemical peculiarities in heterorings of the LXVII-LXXII type and the extensive possibilities of ^1H, ^{13}C, and ^{31}P NMR spectroscopy in this area can be disclosed only in a separate complete review.

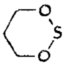
The conformations of propanediol-1,3-sulfite (LXXIII) [269-286], propanediol-1,3-sulfate (LXXIV) [284], 1,3,2-dioxathiane (LXXV) [284, 285], and propanediol-1,3-selenite (LXXVI) have been studied extremely thoroughly by ^1H NMR spectroscopy. The ^{13}C NMR spectra of some of them have been investigated [285], the possible reasons for stabilization of the axial orientation of the S=O and Se=O bonds [278] and the chemical evidence for the axial orientation of S=O [277] have been discussed, and a $\Delta G_{SO_a}{}^{\circ}$ value of 9.03 kJ-mole^{-1} has been determined [286]. The problem of the contribution of the twist forms in 4,6-substituted sulfites has been examined in detail [280, 284, 287].



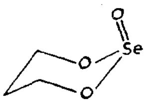
LXXIII



LXXIV



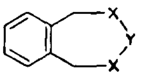
LXXV



LXXVI

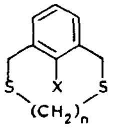
Heterorings with More than Six Atoms in the Ring

The topology of interconversion and pseudorotation in rings with more than six atoms has been analyzed thoroughly [288, 289], however, the introduction of heteroatoms and partially conformation-fixing fragments in the ring, as in the case of LXXVII-LXXX [290-295], and substituents [296-299] simplifies their conformational behavior markedly. The ^1H and ^{13}C NMR spectra of 1,3-dioxa-5,6-benzocycloheptene (LXXVII, X = O, and Y = CH_2) show that an exchange process of the chair—chair type exists at room temperature, however, lines that can be assigned to the chair (79%) and twist (21%) forms appear in the spectrum at −135°C, whereas one twist form was noted in the case of 2-methoxy-1,3-dioxa-5,6-benzocycloheptane [290]. The barrier to ring interconversion in dithiametacyclophanes LXXVIII (X = H, F, Cl, Br, n = 2-6) [293] increases as the volume of X increases and n decreases. According to ^1H and ^{13}C NMR data, in compounds of the LXXIX type the observed intramolecular process is explained by a dissociative-inversion mechanism, which is characterized by $\Delta G^{\neq} = 65.3$ kJ-mole^{-1} when R = R' = CH_3 and $T_C = 41.0°C$ [294]. The anti conformation is dominant in macrocycles LXXX at room temperature, whereas the syn conformation is dominant at temperatures below −70°C [295].

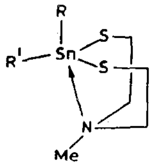


X = O,S ;
Y = CH_2, S; S = O; Se = O

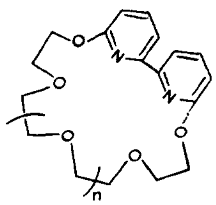
LXXVII



LXXVIII



LXXIX



n = 0 - 4

LXXX

The configurations and conformations of stereoisomeric 4-alkyl-6-methoxy-1,3-dioxepanes [296-298] and 2,3-dihydro-1H-1,4-diazepinium salts [300] have been investigated.

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