1,3-Dimethyl-2-(5'-methyl-2'-furyl)benzimidazolium Perchlorate (XVI). A 5-ml sample of a 60% solution of perchloric acid was added to a boiling solution of 3.54 g (10 mmole) of the methiodide of V in 100 ml of water, and the precipitated perchlorate was removed by filtration to give 2.64 g (81%) of colorless crystals with mp 208-209°C (from water). Found: N 8.2%. $C_{14}H_{15}ClN_2O_5$. Calculated: N 8.5%.

1,3-Dimethyl-2-(5'-methyl-4'-bromo-2'-furyl)benzimidazolium Perchlorate (XVII). A 3.26-g (10 mmole) sample of XVI was dissolved in 50 ml of dichloroethane, 3.2 g (20 mmole) of bromine was added, and the mixture was heated at 80°C for 6 h. The solvent was then evaporated, and the reaction product was dissolved by heating in water containing a small amount of propyl alcohol. Cooling of the solution produced yellowish needles with mp 223-224°C. The yield was 2.9 g (72%). Found: C 41.8; H 3.2; N 7.1%. $C_{14}H_{14}BrClN_2O_5$. Calculated: C 41.4; H 3.5; N 6.9%.

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CONFORMATION OF 1,2,3,4-TETRAHYDRO-2-PYRIMIDINONES

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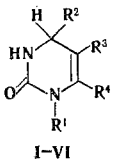
The conformation of a number of 1,2,3,4-tetrahydro-2-pyrimidinones with various substituents in the ring was established on the basis of the vicinal $^3J_{34}$ constants found from the ^1H NMR spectra of these compounds. It is shown that in solution rapid conformational transformations between the two possible "boat" conformations evidently occur.

Compounds I-VI have been examined to establish the conformation of 1,2,3,4-tetrahydro-2-pyrimidinones by NMR spectroscopy [1-4]. The parameters of the spectra of these compounds are presented in Table 1. A vicinal spin–spin coupling constant (SSCC) between the 3-H and 4-H protons, the magnitude of which ranged from 1.5 to 3.2 Hz and depends on the HN_3C_4H dihedral angle, is observed in the spectra.

The NH_3C_4H fragment can be formally regarded as an analog of a cis-peptide bond, for which a dependence of $^3J_{HNCH}$ on the dihedral angle has been found in 5- and 6-membered



I-VI

I $R^1=R^2=R^4=H$, $R^3=COOEt$; II $R^1=H$, $R^2=Ph$, $R^3=COOEt$, $R^4=Me$; III $R^1=R^4=Me$, $R^2=Ph$, $R^3=COOEt$; IV $R^1=R^4=Me$, $R^2=Ph$, $R^3=COOH$; V $R^1=Me$, $R^2=Ph$, $R^3=COOEt$, $R^4=H$; VI $R^1=R^4=Me$, $R^2=Ph$, $R^3=H$

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TABLE 1. Parameters of the PMR Spectra of Tetrahydropyrimidinones I-VI

Compound	Solvent	δ, ppm										Reference
		1-H	3-H	4-H	6-H	1-CH_3	6-CH_3	5-OCH_2	$-CH_3$(Et)	4-C_6H_5	J_{34}	
I	DMSO	8,90	7,05	4,01	7,20	—	—	4,17	1,27	—	1,5[a]	1
II	DMSO	9,13	7,63	5,18	—	—	2,25	3,98	1,08	7,27	2,8	2
III	DMSO	—	7,88	5,15		3,08	2,48	4,01	1,09	7,24	3,2	3
IV	$CDCl_3$	—	6,53	5,38	—	3,17	2,49	—	—	7,24	3,5	4
V	DMSO	—	7,76	5,14	7,50	3,10	—	4,00	1,10	7,28	2,7	
VI[b]	$CDCl_3$	—	5,10	4,61	—	3,12	1,90	—	—	7,29	2,3	4

[a] $^3J_{16}$ = 6.0 Hz. [b] J_{45} = 3.5 Hz; δ_{5-H} 5.02 ppm.

cyclopeptides [5]. The application of this dependence to $^3J_{34}$ for the I-VI molecules (without allowance for the contribution of the C_5—C_6 π-electron bond) gives a dihedral angle of 50-60°. Since the N_3 atom should have sp^2 hybridization, this angle corresponds to the planar I-VI molecules.

However, a study of Dreiding models shows that the I-VI molecules cannot be planar and that the dihedral angle indicated above should be ∿30 or 90°. Agreement between the experimental value and the values obtained from Dreiding models can be reached if it is assumed that conformational transitions that average all of the dihedral angles exist in the I-VI molecules. The gradual increase in $^3J_{34}$ in the order I < VI < V < II < III < IV probably constitutes evidence for an increase in the fraction of the conformer with a pseudoaxial or a boat-axial orientation of the phenyl ring, which increases symbatically with the number of substituents in the ring. The small $^3J_{45}$ value for VI is also in agreement with the conclusion regarding rapid conformational transitions. However, the conformational transitions do not lead to averaging of $^3J_{16}$ in tetrahydropyrimidine I, since they are accomplished between conformations with identical dihedral angles (∿30°).

Thus the 1,2,3,4-tetrahydro-2-pyrimidinone molecules in solutions are not planar and probably exist in a state of conformational transitions of the "boat—boat" type.

EXPERIMENTAL

The NMR spectra of solutions of the compounds in d_6-DMSO and $CDCl_3$ were recorded with a Bruker WH-90 spectrometer with tetramethylsilane as the internal standard.

1-Methyl-4-phenyl-5-ethoxycarbonyl-1,2,3,4-tetrahydro-2-pyrimidinone (V). A mixture of 1.48 g (0.02 mole) of methylurea, 2.1 g (0.02 mole) of ethyl propiolate was refluxed in 50 ml of acetic acid for 3 h, after which the mixture was evaporated, and the residue was crystallized from alcohol to give 4.42 g (85%) of a colorless substance with mp 171-173°C. Found: C 64.8; H 6.0; N 11.0%. $C_{14}H_{16}N_2O_3$. Calculated: C 64.6; H 6.2; N 10.8%.

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