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^{1}H NMR SPECTRA, CONFIGURATION, AND CONFORMATIONS OF 2-MONO- AND 2,4-DISUBSTITUTED 1,3-DIOXOLANES

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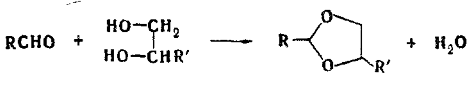
The stereochemistry of 2-furyl-substituted 1,3-dioxolanes was studied. The ethane fragment of 2-monosubstituted dioxolanes displays the spectrum that is typical for an AA'BB' spin system, while the spectra of the 2,4-disubstituted compounds are typical for an ABC system. The contribution of the various conformational forms to the pseudorotation cycle of the dioxolanes is discussed on the basis of an analysis of the spectra by means of an iteration program.

We have used ^{1}H NMR spectroscopy and the $^{3}J_{HH}$, vicinal constants to examine the static stereochemistry of the previously uninvestigated 1,3-dioxolanes. A new approach proposed by one of the co-authors [1] was used in the analysis of the vicinal constants.

1,3-Dioxolanes I-VI (Table 1) were synthesized by the method in [2] by condensation of furfural, furylacrolein, and 3-(5-methyl-2-furyl)propanal with 1,2-diols:



I–VI

I R = furyl, R' = H; II R = 2-[2-(5-methyl-2-furyl)ethyl], R' = H; III R = furyl, R' = CH_3; IV R = 2-[2-(5-methyl-2-furyl)ethyl], R' = CH ; V R = 2-[2-(2-furyl)vinyl], R' = CH_3; VI R = 2-[2-(2-furyl)vinyl], R' = C_6H_5.

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TABLE 1. 1,3-Dioxolanes

Compound	bp, °C (mm)	n_D^{20}	d_4^{20}	Found, %		Empirical formula	Calc., %		Yield, %
				C	H		C	H	
I	75 (5)	1,4815	1,1675						84
II	85 (2)	1,4790	1,0825	65,7	7,7	$C_{10}H_{14}O_3$	65,9	7,8	80
III	70 (7)	1,4745	1,1224						80
IV	97 (7)	1,4740	1,0464	67,2	8,3	$C_{11}H_{16}O_3$	67,3	8,2	77
V	92 (1)	1,5310	1,1350	67,9	4,9	$C_{10}H_9O_3$	67,8	5,1	75
VI	182 (4)	1,5748	—	74,6	5,7	$C_{15}H_{14}O_3$	74,4	5,8	78

TABLE 2. Chemical Shifts and Spin-Spin Coupling Constants of 2-Mono- and 2,4-Disubstituted 1,3-Dioxolanes

Compound	δ, ppm										J_{HH}, Hz
	H_A	$H_{A'}$	H_B	$H_{B'}$	H_C	4-CH_3	$(CH_2)_2$	CH_3	H_a	furyl	
I	3,86	3,86	4,02	4,02	—	—	—	—	5,8	H_α 7,33 $H_{\beta,\beta'}$ 6,27	$^2J_{AB} = {}^2J_{A'B'} = -7{,}7$; $^3J_{AA'} = {}^3J_{BB'} = 7{,}15$; $^3J_{A'B} = {}^3J_{AB'} = 6{,}0$
II	3,685	3,685	3,81	3,81	—	—	α-CH_2 1,82 β-CH_2 2,59	2,21	4,75	5,68	$^2J_{AB} = {}^2J_{A'B'} = -7{,}63$; $^3J_{A'B} = {}^3J_{AB'} = 6{,}05$; $^3J_{AA'} = {}^3J_{BB'} = 7{,}23$; $^3J_{aH} = 4{,}3$; $^3J_{HH} = 7{,}8$
III	3,4	3,4	3,96	3,96	4,22	1,3	—	—	5,72	H_α 7,26 $H_{\beta,\beta'}$ 6,23	$^3J_{HCH_3} = 6{,}0$
cis-IV	3,21	—	3,77	—	4,0	1,18	α-CH_2 1,84 β-CH_2 2,58	2,14	4,76	5,70	$^2J_{AB} = -6{,}5$; $^3J_{BC} = 6{,}5$; $^3J_{AC} = 6{,}5$; $^3J_{aH} = 4{,}5$; $^3J_{HCH_3} = 6{,}0$; $^3J_{HH} = 7{,}8$
trans-IV	3,23	—	3,77	—	4,06	1,14	α-CH_2 1,84 β-CH_2 2,58	2,14	4,88	5,70	
cis-V	3,4	—		—		1,28	—	—	5,31	H_α 7,33 $H_{\beta,\beta'}$ 6,29	$^3J_{DD'} = 16{,}0$; $^3J_{aD} = 5{,}0$; $^3J_{HCH_3} = 6{,}0$; $\delta_{H_D} = 6{,}0$ ppm $\delta_{H_{D'}} = 6{,}48$ ppm
trans-V	3,32	—		—		1,24	—	—	5,48	H_α 7,33 $H_{\beta,\beta'}$ 6,29	
cis-VI	4,11	—	3,58	—	4,92	~7,18*	—	—	5,45	H_α 7,17 $H_{\beta,\beta'}$ 6,23	$^3J_{DD'} = 15{,}0$; $^3J_{aD} = 5{,}0$; $^2J_{AB} = -8{,}0$
trans-VI	4,27	—	3,64		4,98	~7,18*	—	—	5,64	H_α 7,17 $H_{\beta,\beta'}$ 6,23	$^3J_{AB} = -8{,}0$; $^3J_{AC} = 6{,}0$; $^3J_{BC} = 7{,}0$; $^3J_{DD'} = 15{,}0$; $^3J_{aD}$ 5,0

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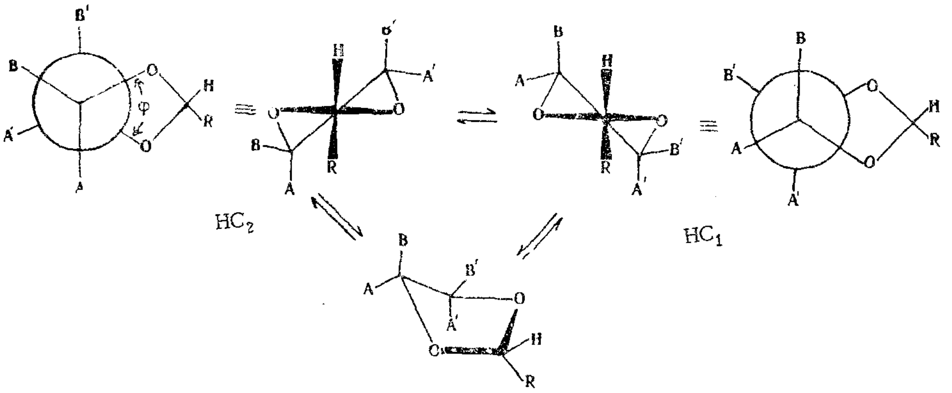
*This is the shift of the protons of the phenyl group.

The absorption bands at 3100, 1500-1600, 1200, and 700-900 cm^{-1} in the IR spectra of II and IV-VI, which were obtained for the first time in this research, indicate the presence of a furan ring, while the four to five bands at 1040-1200 cm^{-1} indicate the presence of an acetal fragment. The stretching vibrations of a double bond appear at 1670 cm^{-1} for V and VI. Characteristic absorption bands of a furan ring (216 nm for acetals II and IV) and of a furylvinyl chromophore (269 nm for dioxolanes V and VI) are present in the UV spectra.

The ^1H NMR spectral parameters for dioxolanes I-VI, viz., the proton chemical shifts and the vicinal $^3J_{HH'}$ spin-spin coupling constants (SSCC), are summarized in Table 2. Because of the chiral character of the C_2 atom, the protons of the 4- and 5-CH_2 groups in I and II form a spin system of the AA'BB' type, the analysis of which we carried out by means of the NMRCAL iteration program with a BNC-12 computer. Because of the chiral character of the C_4 atom, the protons of the 4-CH and 5-CH_2 groups in 4-substituted ($R' = CH_3$ and C_6H_5) dioxolanes display the ^1H NMR spectrum of an ABC spin system, which was also analyzed by means of an iteration program.

Conformation of the Five-Membered Heteroring in 2-Monosubstituted 1,3-Dioxolanes

When one substituent is attached to the C_2 atom, regardless of its size, the heteroring ethane fragment displays the symmetrical spectrum that is typical for an AA'BB' spin system. The lines were assigned to the H_A and H_B protons on the basis of the γ-syn effect (1,3 interaction) of the substituent attached to the C_2 atom [3-5]. It is apparent from the data in Table 2 that the vicinal $^3J_{AA'}$ cis constant is equal to $^3J_{BB'}$ (7.23 Hz), while the vicinal $^3J_{A'B}$ trans constant is equal to $^3J_{AB'}$ (6.05 Hz). However, a similar ratio of the cis and trans constants was found in 2-substituted 1,3-dioxolanes [4]. These values of the constants constitute evidence for rapid pseudorotation of the ring. This can be understood if one takes into account the fact that vicinal cis constant $^3J_{HH'} = 5.40$-6.43 Hz in 2-methyl-trans-2-phenyl-cis-4,5-dimethyl-1,3-dioxolane,* which exists in a state of rapid conformational equilibrium of the $HC_1 \rightleftharpoons HC_2$ type [3] (see the scheme presented below).



On the other hand, the vicinal trans constant is equal to $^3J_{HH'}$ ($^3J_{AB'} = 8.3$ Hz) in trans-4,5-dimethyl-1,3-dioxolane, the molecules of which are characterized by the preferred HC_1 half-chair conformation [3]. Consequently, the $^3J_{A'B}$ trans constant of 6.05 Hz observed in our case is evidently reduced due to the contribution of other forms. If one assumes a conformational transition only between two forms HC_1 (50%) $\rightleftharpoons$ HC_2 (50%), one may write the following expression:

$$6{,}05\ \text{Hz} = 0{,}5\left[{}^3J_{AB'}(HC_1) + {}^3J_{AB'}(HC_2)\right] = 4{,}15 + 0{,}5\,{}^3J_{AB'},$$

from which we find that $^3J_{AB'} = {}^3J_{ee}(HC_2) = 3.8$ Hz.

In addition, according to the Karplus dependence for vicinal constants, the $^3J_{ee}$ value could have been estimated for the HC_2 form if dihedral angle θ between the interacting C–H bonds could have been found. Angle θ is apparently determined by torsion angle ψ (see the scheme presented above). This angle can be estimated within a zero-order approximation by the R-factor method [1]. For II we have $R = 0.84$, and $\psi \approx 42°$. When we find $\theta = 282°$ and subsequently, with allowance for the electronegativities (EN) and orientation of the oxygen and carbon atoms from the modified Karplus expression [1]

$$^3J_{HH'} = (10{,}6\cos^2\theta + 1{,}5\sin^2 2\theta)\left(1 - \sum_i \lambda_i^{\varphi}\Delta E_i\right),$$
$$0° \leqslant \theta \leqslant 90°,\ 270° \leqslant \theta \leqslant 360°,$$

where λ_i^{φ} is a parameter that characterizes the orientation of substituent X (oxygen and carbon) through phase angle $\varphi_{XH} = \theta - 120°$, and ΔE_i is the difference in the electronegativities of substituent X and the hydrogen atom on the Higgins scale, we find $^3J_{ee} = 0.33$ Hz, i.e., a considerably smaller value than $^3J_{AB'} = 3.8$ Hz, which was found for the hypothetical exchange process of the $HC_1 \rightleftharpoons HC_2$ type.

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*Let us note that in a second publication, presented in the form of reference [3], Anteunis and Alderweireldt arrived at an erroneous assignment of the configuration of this compound (see [5]).

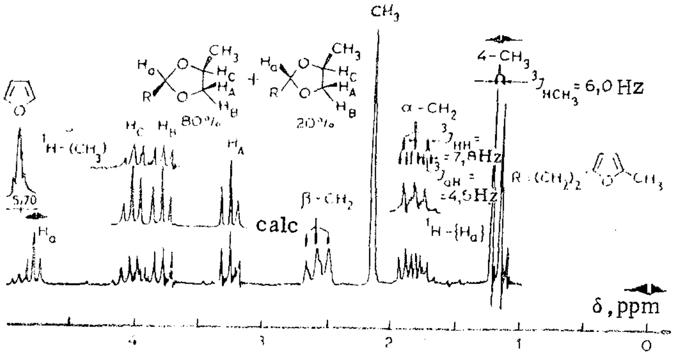

Fig. 1. ^{1}H NMR spectrum, total ^{1}H-{CH$_3$} nuclear double magnetic resonance spectrum and calculated spectrum of the ABC protons of cis-2-[2-(5-methyl-2-furyl)ethyl]-4-methyl-1,3-dioxolane (IV).

This result indicates that many other forms in addition to the HC$_1$ and HC$_2$ forms are involved in the pseudorotation cycle.

Configuration and Conformation of 2,4-Disubstituted 1,3-Dioxolanes

It is known that replacement of one of the valences of any endocyclic carbon atom in six-membered 1,3-diheterocycles shifts the conformational equilibrium sharply to favor one preferred chain conformation [6]. The freedom of rapid pseudorotation is retained in 1,3-dioxolanes, despite substitution in the 2 and 4 positions. This can be seen from the ^{1}H NMR spectrum of IV, which is presented in Fig. 1. The spectrum of IV shows above all that the sample is a mixture of two configurational isomers (cis and trans) in a ratio of 80:20. This can be seen from the two triplet lines at δ 4.76 and 4.88 ppm, which belong to the methylidyne 2-H$_a$ proton. On the basis of the γ effect [3, 5], the triplet at δ 4.76 ppm (at higher field) can be assigned to the cis isomer, and it is obtained in larger amounts (~80%) as a result of synthesis and distillation. It should be noted here that the cis-trans equilibrium in 2,4-disubstituted 1,3-dioxolanes was the subject of a special study [7, 8] by gas-liquid chromatography (GLC), and it was shown that the cis:trans ratio is close to 3:2, depends on the nature of the substituents, and reaches 4:1 when R = tert-Bu [8].

In the case of 4-methyl-substituted 1,3-dioxolanes III-V the spectrum of the ring protons corresponds to a six-spin system of the ABCM$_3$ type. To simplify the calculation we examined the ABC system and compared the result with the experimental spectrum recorded under the conditions of homonuclear total double resonance of the ^{1}H-{CH$_3$} nuclear magnetic double resonance type (Fig. 1). In the case of IV, as seen from the data in Table 2, vicinal trans constant $^3J_{BC}$ is 6.5 Hz, which coincided with cis constant $^3J_{AC}$ = 6.5 Hz. This result, in conformity with the estimate of trans constant $^3J_{ee}^{calc}$ = 0.33 Hz and $^3J_{AB}^{exp}(HC_1)$ = 8.3 Hz, makes it possible to assert that rapid conformational isomerization also occurs in the case of disubstituted 1,3-dioxolanes however, the composition of the contribution of the other forms is different than in the case of the monosubstituted compounds. If one nevertheless assumes reversible exchange of the HC$_1 \rightleftarrows$ HC$_2$ type, from the expression

$$^3J_{BC}{}^{exp} = {}^3J_{AB}{}^{exp}\varkappa + {}^3J_{ee}{}^{calc}(1-\varkappa),$$

one can find the fraction of the pseudoequatorial (CH$_3$) HC$_2$ conformation, which is $\varkappa$ = 0.79, i.e., the conformational equilibrium is shifted to favor the preferred half-chair conformation with a pseudoequatorial methyl group. A similar conclusion regarding the preferred pseudoequatorial orientation of the ClCH$_2$ group was recently drawn in [5], in which 2-trifluoromethyl-4-chloromethyl-1,3-dioxolane was studied by ^{1}H NMR spectroscopy at 300 MHz. If one takes into account the fact that because of the orientational contribution of the oxygen atoms, the numerical value of the trans constant of the $^3J_{ee}$ type in forms that differ from the HC form has a greater value, the fraction of the contribution of the HC$_2$ conformation in the actual pseudorotation cycle should be less than 79% but is nevertheless still the dominant contribution.

EXPERIMENTAL

The ^1H NMR spectra of 5% (by volume) solutions of the compounds in CCl_4 were recorded with a Varian HA-100D spectrometer at 29°C with tetramethylsilane as the internal standard. The IR spectra of films of the compounds between NaCl plates were recorded with a Specord 71-IR spectrometer with an NaCl prism. The UV spectra of aqueous solutions of the compounds in 10-mm thick quartz cuvettes were recorded with a Specord UV-vis spectrophotometer.

2-Furyl-4-phenyl-1,3-dioxolane (VI). A mixture of 6.01 g (0.05 mole) of furylacrolein, 6.9 g (0.05 mole) of phenylethylene glycol, 1.5 g of KU-2 cation-exchange resin in the H^+ form, and 80 ml of benzene was refluxed for 3-4 h in a three-necked flask equipped with a stirrer, a Dean–Stark apparatus, and a reflux condenser. After decantation and removal of the solvent by distillation, the reaction product was isolated by vacuum frationation to give 8.5 g of dioxolane VI.

Compounds I-V were similarly obtained.

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MESOIONIC COMPOUNDS WITH A BRIDGED NITROGEN ATOM. 5.* π-ELECTRON STRUCTURE OF THIAZOLO[3,2-*a*]PYRIDINIUM 3-OXIDE DERIVATIVES

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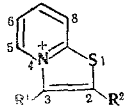
The π-electron structure of thiazolopyridinium derivatives was analyzed thoroughly by the methods of quantum chemistry in order to ascertain the reason for the development of colors in the case of mesoionic compounds.

Despite the fact that mesoionic compounds have been known for a relatively long time [2], the reasons responsible for their deep coloration have thus far remained unclear [3]. It therefore seemed of interest to thoroughly analyze the π-electron structures of such compounds by means of the methods of quantum chemistry. Such calculations of mesoionic compounds have already been made (see [2]); however, only certain properties of the ground state were discussed.

In the present research we performed quantum-chemical calculations of the model systems the thiazolo[3,2-*a*]pyridinium cation (I), thiazolo[3,2-*a*]pyridinium 3-oxide (II), and the 3-methoxythiazolo[3,2-*a*]pyridinium cation (III) in order to determine the electron distribution in both the ground and excited states and to ascertain the reasons for the development of coloration in compounds of the II type.



III

I $R^1=H$, $R^2=H$;
II $R^1=O^-$, $R^2=H$;
III $R^1=OCH_3$, $R^2=C_6H_5$.

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[*] See [1] for communication 4.

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