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STEREOSTRUCTURE OF 2-ETHYNYL-SUBSTITUTED 2,4,4-TRIMETHYL-1,3-DIOXANES

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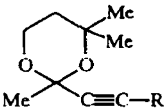
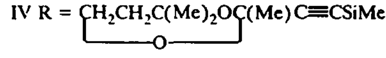
It has been shown by PMR spectrometry and x-ray structure analysis that the six-membered 1,3-dioxane ring of 2-ethynyl-substituted 2,4,4-trimethyl-1,3-dioxanes, either in solution or in the solid state, exists in a nearly ideal chair conformation with an axial position of the ethynyl substituent.

Certain compounds that we had synthesized previously [1-3], 2-ethynyl-substituted 2,4,4-trimethyl-1,3-dioxanes (I-IV), are of interest not only as predecessors of α-acetylene ketones [3], but also as models for studying the influence of substituents in positions 2 and 4 on the conformation of the six-membered ring.



I-IV

I R = Ph; II R = Me_3Si; III R = $CH{\equiv}CSiMe_2$;



IV R = $CH_2CH_2C(Me)_2OC(Me)C{\equiv}CSiMe_2$

The spatial structure of compounds I-IV was established by PMR spectrometry. The parameters of the spectra are listed in Table 1. Analysis of the values of the chemical shift and spin–spin coupling constants indicates that all of the compounds of this series exist predominantly in the chair conformation, since there is a phenomenon of inversion of chemical shifts of the methylene protons at the $C_{(5)}$ atom (Table 1). This is explained mainly by a charge displacement effect [4] that is characteristic for compounds with heteroatoms carrying an unshared electron pair, with an upfield shift experienced by the 5-H_e proton in the anti position relative to the heteroatom [5]. It should be noted that the difference in chemical shifts of the axial and equatorial protons in position 5 ($\Delta\delta_{5a5e}$) is considerably smaller than for the analogous protons of 1,3-dioxane (−0.72 ppm) [6], with the following values (in ppm): Compound I, 0.35 ($CDCl_3$) and 0.45 (CD_2Cl_2 + CCl_4); compound II, 0.40 (CCl_4); compound III, 0.16 (CCl_4); compound IV, 0.60 [$(CD_3)_2CO$] and 0.20 (CD_2Cl_2) (see Table 1). The decrease in values of $\Delta\delta_{5a5e}$ is related to the influence of the two methyl groups in the β-position relative to the 5-H_a and 5-H_e protons, with the β-effect being particularly significant for the axial proton. In 1,3-dioxanes, an equatorial methyl group shifts the signal of the ring proton in the β-position relative to the methyl group, with an upfield shift of 0.4 ppm; and as a consequence, inversion of chemical shifts of the axial and equatorial protons in position 5 cannot be observed [6].

In the case of the methylene protons H_A and H_B at the $C_{(6)}$ atom, we also observe inversion of the nuclear magnetic screening constants and significant values of $\Delta\delta_{HAHB}$ (from 0.42 to 0.60 ppm; see Table 1), which is a characteristic indicator for 1,3-dioxanes in the chair conformation [6]. The assignment of signals to the axial and equatorial protons was made on the basis of an analysis of parameters of the four-spin system ABXY and the substantial difference in values of the SSCC $^3J_{Aa}$ (11.7-12.3 Hz) and $^3J_{Ba}$ (5.0-5.5 Hz) (Table 1). At the $C_{(4)}$ atom, the protons of the gem-dimethyl grouping also

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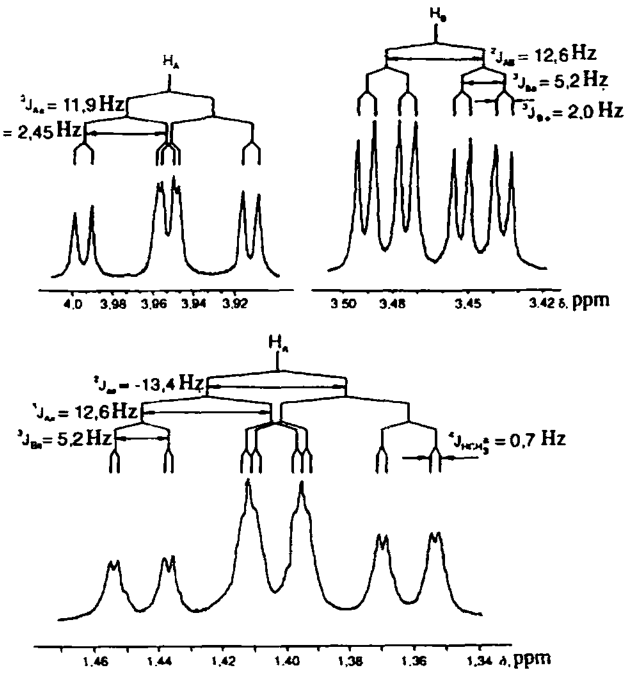


Fig. 1. Fragments of PMR spectrum of dimethyl-bis[(2,4,4-trimethyl-1,3-dioxanyl-2)-ethynyl]silane, taken in $(CD_3)_2CO$.

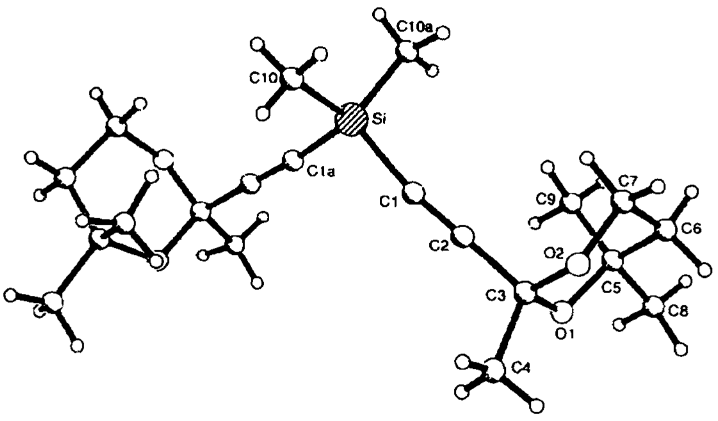
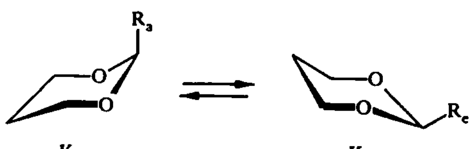


Fig. 2. Structure of the 1,3-dioxane IV as determined by x-ray structure analysis.

experience inversion of chemical shifts with rather large values of $\Delta\delta_{Me}a_{Me}e$ (−0.33 : −0.67 ppm); here, the signal of the axial methyl is broadened in comparison with that of the equatorial methyl as a consequence of spin−spin coupling with the 5-H_a proton. Usually, the value of the long-range SSCC $^4J_{HCCCH3}$ is about 0.8 Hz [7]; for compound IV, it is equal to 0.7 Hz (Fig. 1). In principle, inversion of chemical shifts of protons in position 6 and the gem-dimethyl grouping at the $C_{(4)}$ atom in six-membered heterocycles is used as a criterion of the axial position of the substituent at the $C_{(2)}$ atom. In the series of compounds I-IV, there are two substituents in this position, i.e., a CH_3 group and an ethynyl-containing fragment. It has been shown by numerous physicochemical studies of 2-methyl-substituted cyclohexanes and 1,3-dioxanes that a two-component equilibrium is realized in solution, between identical conformational structures — the chair-a (K_a) and the chair-e (K_e), with the axial conformer accounting for 4% [8, 9].



K_a K_e

A study of the influence of temperature in the case of 5,5-dimethyl-1,3-dioxane with a C≡CH at the $C_{(2)}$ atom of the ring, by means of dynamic ^1H and ^{13}C NMR, revealed a predominance of the chair-axial conformer K_a, with a value of ΔG_{283} in $(CD_3)_2CO$ equal to 1.81 kJ/mole [10]. In this case (and also for compounds I-IV), the reason for the inversion of chemical shifts of the protons at the $C_{(4)}$ and $C_{(6)}$ atoms may be the magnetically anisotropic and electrical effects of the axial C≡C bond in the chair conformation K_a, the same as in cyclic esters and sulfites [7]. Nonetheless, according to data on the influence of the solvent on conformational equilibrium in solutions of similar compounds [10], we cannot eliminate the possibility of a certain contribution of the K_e form. This is supported by the fact of change in magnitude of the SSCC (geminal and vicinal) when the solvent is changed in the case of compounds I and IV (Table 1).

In Fig. 1 we show part of the ^1H NMR spectrum of compound IV, in which there are signals of the protons at the $C_{(5)}$ (H_a) and $C_{(6)}$ atoms.

The region of resonance of A,B-protons shows up as a typical spectrum of an ABXY system, where the values of the SSCC are strictly stereospecific within the framework of a chairlike conformation of the 1,3-dioxane systems [7]: $^2J_{AB} \sim {}^3J_{Aa}$ (−12.6, 11.9 Hz), $^3J_{Ba} \sim 1/2\ {}^3J_{Aa}$ (5.2, 11.9 Hz), $^3J_{Ae} > {}^3J_{Be}$ (2.45, 2.0 Hz). The more complex form of the multiplet pertaining to the 5-H_a proton is due to its long-range spin−spin coupling with the protons of the axial methyl group in position 4 ($^4J_{HCCCH3}$, 0.7 Hz). The value of $\Delta\delta_{AB}$, 0.5 ppm, is higher than for 1,3-dioxane (0.34 ppm) and is somewhat lower than the analogous value in cyclohexane (0.55 ppm) [6]. The value of the geminal constant $^2J_{AB} = -12.6$ Hz, which is extremely sensitive to the stereochemistry of six-membered heterocycles, is 0.45 Hz lower than the value for the methylene fragment in cyclohexane. According to the theory set forth in [11], the geminal constant $^2J_{HH}$ in CH_2X fragments will depend on the C−H bonds and on the relative position of the unshared electron pair of X, which is related to the cyclic torsion angle φ. By using plots of Δ^2J_{HH} as a function of φ, we can estimate the torsion angle of a fragment containing a heteroatom with an unshared electron pair. In the present case, this angle is ~56°; i.e., the carbon part of the ring is somewhat flattened in comparison with cyclohexane (58°) [12]; according to data reported in [6, 13], this is the reason for the decrease in magnitude of nonequivalence of chemical shifts of the A,B-protons (in comparison with cyclohexane). A more precise evaluation of the torsion angles can be made by means of the R-factor, since its use requires values of all four SSCCs $^3J_{HH}$. Values calculated for the R-factor [13] and the corresponding torsion angles that are listed in Table 1 demonstrate structural uniformity of compounds I-IV, and these values are in good agreement with data obtained for 1,3-dioxanes by x-ray diffraction [7].

In order to confirm these results and to study 2-ethynyl-substituted 1,3-dioxanes, with the aim of investigating the conformation of the 1,3-dioxane ring and the position of the ethynyl fragment relative to this ring, we investigated the molecular-crystal structure of the 1,3-dioxane IV by x-ray diffraction. In Fig. 2 we illustrate the geometry of a three-dimensional model of the molecule of dimethyl-bis[(2,4,4-trimethyl-1,3-dioxanyl-2)ethynyl]silane (IV). The coordinates of the atoms, the bond lengths, bond angles, and torsion angles are listed in Tables 2-5. The 2,4,4-trimethyl-1,3-dioxanyl-2-ethynyl fragments are absolutely identical; therefore, in the subsequent discussion, we will consider only one of these fragments. In most cases, the interatomic distances and the bond angles match the standard values [14]. An exception is found in the system of atoms $Si-C_{(1)}\equiv C_{(2)}-C_{(3)}$. The linearity of this fragment is disrupted, since the angles $Si-C_{sp}\equiv C_{sp}$ and $C_{sp}\equiv C_{sp}-C_{sp3}$ are equal to 171.2° and 178.8°, respectively, and their change is due to steric strain at the tetracoordinated silicon atom. This view is further supported by the change in bond lengths. Whereas the length of the $Si-C_{sp3}$ bond (1.838 Å) is close to the standard value, the length of the $Si-C_{sp}$ bonds (1.835 Å) is significantly higher (by 0.033 Å) in comparison with the bond of methylethylsilane, ($d_{Si}-C_{sp}$* = 1.802 Å) [15]. The same sort of lengthening of the $Si-C_{sp}$ bond to 1.829 Å and 1.851 Å ($d_{Si}-C_{sp}$* 0.020 and 0.049 Å) had been established by x-ray diffraction measurements for the molecules of 1,8-bis(trimethylsilyl)octatetrayne [16] and bis[di(tert-butyl)tert-butylamino]silylacetylene [17].

The 1,3-dioxane ring has the conformation of a slightly distorted chair (folding parameters [18] $S = -1.105$, $\theta = 6.41°$, $\varphi_2 = 90.79°$).

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*Notation as in Russian original: there are apparent errors in the notation and also possibly in the values — Translator.

TABLE 1. PMR Spectra of 2-Ethynyl-Substituted 2,4,4-Trimethyl-1,3-dioxanes

Compound	Solvent	Chemical shift δ, ppm								SSCC (J), Hz						R-factor	Torsion angle φ
		2-Me	4-Me_a	4-Me_e	5-H_a	5-H_e	6-H_a	6-H_B	R	$^2J_{AB}$	$^2J_{ae}$	$^3J_{Aa}$	$^3J_{Ae}$	$^3J_{Ba}$	$^3J_{Be}$		
I	$CDCl_3$	1,73	1,64	1,23	1,75	1,40	4,37	3,85	7,05	-12,3	-14,1	12,3	2,6	5,5	2,1	1,7735	55°00
	$CD_2Cl_2 + CCl_4$	1,47	1,35	0,98	1,60	1,15	4,24	3,76	7,05	-11,9	—	11,9	2,7	5,1	2,0	1,7700	54°52′
II	CCl_4	1,50	1,48	1,17	1,80	1,40	4,26	3,75	0,29	-11,7	-14,5	11,7	3,1	5,0	2,5	1,7530	54°50′
III	CCl_4	1,23	1,16	0,90	1,06	0,90	4,00	3,40	0,05*	-11,7	-14,5	11,7	3,1	5,0	2,5	1,7530	54°50′
IV	$(CD_3)_2CO$	1,22	1,17	0,83	1,40	1,15	3,90	3,40	0,20*	-12,6	-13,7	11,9	2,45	5,2	2,0	1,8100	55°20′
	CD_2Cl_2	1,16	1,16	0,83	1,30	0,60	3,90	3,38	0,20*	-11,7	—	11,7	3,10	5,0	2,5	1,7530	54°50′

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*Chemical shift of protons of $SiMe_2$ grouping.

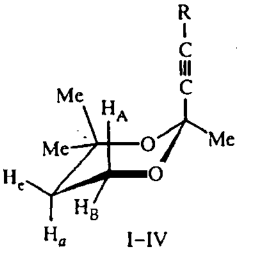
TABLE 2. Coordinates of Atoms in Molecule of the 1,3-Dioxane IV ($\times 10^4$)

Atom	x	y	z
Si	7500(0)	5000(0)	1712(1)
$O_{(1)}$	4943(1)	3581(1)	7358(2)
$O_{(2)}$	5251(1)	3033(1)	4655(2)
$C_{(1)}$	6860(2)	4395(1)	3594(4)
$C_{(2)}$	6326(2)	3998(1)	4705(3)
$C_{(3)}$	5679(1)	3501(1)	6108(5)
$C_{(4)}$	6287(2)	3382(1)	7910(3)
$C_{(5)}$	4077(2)	3560(1)	6118(4)
$C_{(6)}$	3683(2)	3063(1)	4496(4)
$C_{(7)}$	4515(2)	3046(1)	3105(4)
$C_{(8)}$	4338(2)	4099(1)	4850(4)
$C_{(9)}$	3335(2)	3478(1)	8039(5)
$C_{(10)}$	8465(2)	4947(1)	-80(6)

TABLE 3. Bond Lengths (d) in Molecule of the 1,3-Dioxane IV

Bond	d, Å	Bond	d, Å
Si—$C_{(1)}$	1,835(2)	Si—$C_{(10)}$	1,838(4)
Si—$C_{(1a)}$	1,835(2)	Si—$C_{(10a)}$	1,838(4)
$O_{(1)}$—$C_{(3)}$	1,416(3)	$O_{(1)}$—$C_{(5)}$	1,460(3)
$O_{(2)}$—$C_{(3)}$	1,411(2)	$O_{(2)}$—$C_{(7)}$	1,433(3)
$C_{(1)}$—$C_{(2)}$	1,196(2)	$C_{(2)}$—$C_{(3)}$	1,494(2)
$C_{(3)}$—$C_{(4)}$	1,512(4)	$C_{(5)}$—$C_{(6)}$	1,525(3)
$C_{(5)}$—$C_{(8)}$	1,524(3)	$C_{(5)}$—$C_{(9)}$	1,513(4)
$C_{(6)}$—$C_{(7)}$	1,501(4)		

Thus, by means of ^1H NMR spectrometry and x-ray structural analysis, it has been established for the 2-ethynyl-substituted 2,4,4-trimethyl-1,3-dioxanes I-IV that the 6-membered dioxane ring has the chair conformation with an axial position of the ethynyl-containing fragment at $C_{(2)}$ of the ring.



I-IV

EXPERIMENTAL

The PMR spectra of compound I were recorded in Bruker spectrometers (200 and 80 MHz) in $CDCl_3$ and CD_2Cl_2, respectively. The PMR spectra of compounds II-IV were recorded in a Tesla BS-467 spectrometer (60 MHz) in CCl_4 and CD_2Cl_2; the spectrum of compound IV was also recorded in a Varian Unity 300 instrument in $(CD_3)_2CO$. The pulse length was 7.0 μsec, pulse length at 90° 14.2 μsec, depth of sweep 6000 Hz, data memory volume 16 K, scanning time 4.5 sec, lag between pulses 4 sec. Internal standard HMDS.

X-Ray Structure Study of IV. Transparent, colorless, monoclinic crystals of compound IV were grown from 50% aqueous alcohol. Elementary cell constants: a = 14.984(4), b = 27.220(6), c = 5.773(1) Å, γ = 117.19(2)°, V = 2094.4(1.8) Å^3. Space group A2/a, Z = 4, d_{calc} = 1.143 g/cm^3. Cell constants of 1072 independent reflections with I >

TABLE 4. Bond Angles (ω) in Molecule of the 1,3-Dioxane IV

Angle	ω (deg)	Angle	ω (deg)
$C_{(1)}$—Si—$C_{(10)}$	111,7(1)	$C_{(1)}$—Si—$C_{(1a)}$	107,4(1)
$C_{(10)}$—Si—$C_{(1a)}$	107,3(1)	$C_{(1)}$—Si—$C_{(10a)}$	107,3(1)
$C_{(10)}$—Si—$C_{(10a)}$	111,5(2)	$C_{(1a)}$—Si—$C_{(10a)}$	111,7(1)
$C_{(3)}$—$O_{(1)}$—$C_{(5)}$	119,0(1)	$C_{(3)}$—$O_{(2)}$—$C_{(7)}$	112,7(2)
Si—$C_{(1)}$—$C_{(2)}$	171,2(2)	$C_{(1)}$—$C_{(2)}$—$C_{(3)}$	178,8(3)
$O_{(1)}$—$C_{(3)}$—$O_{(2)}$	112,2(2)	$O_{(1)}$—$C_{(3)}$—$C_{(2)}$	111,4(2)
$O_{(2)}$—$C_{(3)}$—$C_{(2)}$	109,6(2)	$O_{(1)}$—$C_{(3)}$—$C_{(4)}$	105,7(2)
$O_{(2)}$—$C_{(3)}$—$C_{(4)}$	106,6(2)	$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	111,2(2)
$O_{(1)}$—$C_{(5)}$—$C_{(6)}$	108,2(2)	$O_{(1)}$—$C_{(5)}$—$C_{(8)}$	111,4(2)
$C_{(6)}$—$C_{(5)}$—$C_{(8)}$	112,7(2)	$O_{(1)}$—$C_{(5)}$—$C_{(9)}$	103,1(2)
$C_{(6)}$—$C_{(5)}$—$C_{(9)}$	111,1(2)	$C_{(8)}$—$C_{(5)}$—$C_{(9)}$	109,9(2)
$O_{(5)}$—$C_{(6)}$—$C_{(7)}$	111,5(2)	$O_{(2)}$—$C_{(7)}$—$C_{(6)}$	109,0(2)

TABLE 5. Torsion Angles (τ) in Molecule of the 1,3-Dioxane IV

Angle	τ (deg)	Angle	τ (deg)
$C_{(10)}$—Si—$C_{(1)}$—$C_{(2)}$	-129,7	$C_{(1)}$—$C_{(2)}$—$C_{(3)}$—$O_{(2)}$	-96,8
$C_{(1a)}$—Si—$C_{(1)}$—$C_{(2)}$	111,9	$C_{(1)}$—$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	20,8
$C_{(10a)}$—Si—$C_{(1)}$—$C_{(2)}$	-7,3	$C_{(3)}$—$O_{(1)}$—$C_{(5)}$—$C_{(6)}$	44,8
Si—$C_{(1)}$—$C_{(2)}$—$C_{(3)}$	170,4	$C_{(3)}$—$O_{(1)}$—$C_{(5)}$—$C_{(8)}$	-79,6
$C_{(5)}$—$O_{(1)}$—$C_{(3)}$—$O_{(2)}$	-48,1	$C_{(3)}$—$O_{(1)}$—$C_{(5)}$—$C_{(9)}$	162,5
$C_{(5)}$—$O_{(1)}$—$C_{(3)}$—$C_{(2)}$	75,1	$O_{(1)}$—$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	-48,5
$C_{(5)}$—$O_{(1)}$—$C_{(3)}$—$C_{(4)}$	-164,0	$C_{(8)}$—$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	75,2
$C_{(7)}$—$O_{(2)}$—$C_{(3)}$—$O_{(1)}$	54,7	$C_{(9)}$—$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	-161,0
$C_{(7)}$—$O_{(2)}$—$C_{(3)}$—$C_{(2)}$	-69,6	$C_{(3)}$—$O_{(2)}$—$C_{(7)}$—$C_{(6)}$	-60,5
$C_{(7)}$—$O_{(2)}$—$C_{(3)}$—$O_{(4)}$	170,0	$C_{(5)}$—$C_{(6)}$—$C_{(7)}$—$O_{(2)}$	57,7
$C_{(1)}$—$C_{(2)}$—$C_{(3)}$—$O_{(1)}$	138,4		

3σ(I) were measured in a Nicolet P3 automatic diffractometer (MoKα radiation without monochromator, $\theta/2\theta$ scanning to $2\theta_{\max} = 36°$). The structure was deciphered by the direct method, using the SHELXTL program set [19] and was refined in the anisotropic approximation (isotropic for hydrogen atoms) down to a divergence factor $R = 0.030$, $R_w = 0.033$.

The coordinates of the hydrogen atoms may be obtained from the authors upon request.

The syntheses of the 1,3-dioxanes I, II and III, and IV were performed by procedures given in [2, 3, 1], respectively.

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