

# STEREOCHEMISTRY OF HETEROCYCLES

## VI.\* STUDY OF THE CONFORMATIONS OF 2,5-DIALKYL-1,3-DIOXANES BY MEANS OF DIPOLE MOMENTS

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The conformations of stereoisomeric 2,5-dialkyl-1,3-dioxanes were studied by means of dipole moments (DM), and it was shown that the low-boiling isomers have a chair conformation or a somewhat distorted symmetrical boat conformation, while the high-boiling isomers have a chair conformation with diequatorial orientation of the substituents. The DM measurements lead to values for the ketals which are closest to those calculated for the chair conformation.

2,5-Dialkyl-1,3-dioxanes exist as geometrical isomers which have cis and trans configurations and different conformations. Continuing our previous investigations [1-3], we have studied the conformations of stereoisomeric 2,5-dialkyl-1,3-dioxanes by means of dipole moments (DM). The structures of these compounds were previously studied in detail by NMR spectroscopy by which the configurations of the individual isomers were established, and concepts regarding their various conformations were worked out [4, 5].

2,5-Dialkyl-1,3-dioxanes are simpler compounds than the 2,5-dialkyl-5-alkoxyalkyl-1,3-dioxanes which we initially investigated by NMR and DM methods [2, 3, 6, 7], since they do not contain polar substituents outside of the ring. The DM values in such substances are determined by the conformation of the 1,3-dioxane ring itself.

The experimental DM values of 2,5-dialkyl-1,3-dioxanes (I-VI) and 2,2-dimethyl-5-alkyl-1,3-dioxanes (VII-IX), measured at 25°C in benzene, are presented in Table 1. As seen from these data, all of the compounds of the group under consideration have close DM values (from 1.80 to 2.08 D). In contrast to the previously investigated stereoisomeric 2,5-dialkyl-5-alkoxyalkyl-1,3-dioxanes, no substantial differences in the DM values of the individual isomers are observed in the 2,5-dialkyl-1,3-dioxane series.

The DM values calculated for the various conformations of 1,3-dioxane are given in Table 2. The valence angles, bond lengths, and atomic coordinates presented in [2] were used to calculate the DM. The following bond DM were used: C-O 0.9D and C-H 0.28D [8].

A comparison of the experimental DM of both isomers of acetals I-VI with the calculated values indicates that the DM of the chair and symmetrical boat conformations are closest to the experimental values. It is interesting that the DM of the unsymmetrical boat conformation, which is widely distributed in the 2-substituted 5-alkyl-5-alkoxyalkyl-1,3-dioxane series, like the values calculated for the skew symmetrical boat [1-3], turns out to be considerably lower than the experimental DM value in the investigated I-IX series.

These DM measurements made it possible to draw definite conclusions regarding the configuration and conformation of the compounds examined. First of all, it should be noted that the high-boiling isomers of 2,5-dialkyl-1,3-dioxanes have lower refractive indexes and densities than the low-boiling isomers [4]. This means that they do not obey the Auwers-Skita rule even in its improved form [9]. It should, however,

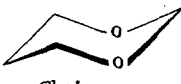
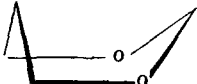

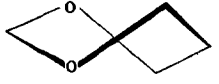
\* See [1] for communication V.

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TABLE 1. Experimental DM Values of 2,5-Dialkyl- and 2,2,5-Trialkyl-1,3-dioxanes

Compound	R	R'	R''	bp, mm	$n_D$	$d_4$	$\alpha$	$\beta$	$MR_D$	$P_{200}$	$\mu, D$
Ib	CH <sub>3</sub>	CH <sub>3</sub>	H	124 (760)	2,2718	0,8734	4,5056	0,0011	31,16	103,97	1,89
IIa	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	H	136,5 (770)	2,2750	0,8725	4,5427	0,1401	35,54	106,98	1,87
IIb				141,9 (770)	2,2756	0,8717	4,4311	0,2230	35,44	102,88	1,82
IIIa	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	H	59,5 (13)	2,2713	0,8728	4,2157	0,0016	39,97	111,17	1,87
IIIb				65,0 (13)	2,2724	0,8729	4,8782	0,0085	40,03	121,21	1,99
IVa	C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	H	51,0 (0,5)	2,2777	0,8733	3,9997	0,0499	53,98	120,84	1,81
IVb				57,5 (0,5)	2,2717	0,8727	5,1041	0,0875	54,11	135,98	1,99
Va	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	H	80,0 (11)	2,2731	0,8734	4,6175	0,1388	49,27	120,84	1,87
Vb				84,5 (11)	2,2775	0,8732	4,0721	0,1064	49,31	115,39	1,80
VIa	C <sub>6</sub> H <sub>13</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	H	71,0 (0,5)	2,2741	0,8732	3,7018	0,0216	63,13	126,898	1,76
VIb				73,5 (0,5)	2,2710	0,8737	5,2156	0,0577	63,35	151,45	2,08
VII	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	39 (13)	2,2738	0,8730	4,9194	0,1138	35,85	113,26	1,94
VIII	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	CH <sub>3</sub>	51 (3)	2,2768	0,8739	4,7602	0,0446	44,82	118,13	1,89
IX	C <sub>6</sub> H <sub>13</sub>	CH <sub>3</sub>	CH <sub>3</sub>	90 (2)	2,2745	0,8726	4,7781	0,1004	58,41	135,61	1,94

TABLE 2. Calculated DM Values

Conformation	$\mu, D$
 Chair	1,90
 Symmetrical boat	1,76
 Unsymmetrical boat	1,22
 Twist conformation	0,96

be remembered that the empirical rules, which are similar to the Auwers-Skita rule, must be used very cautiously, particularly with respect to the boiling points. It has been shown in a number of investigations [10, 11] that the sequence of boiling points of stereoisomeric dialkylcyclohexanes depends on the structure, length, and position of the side substituents.

A boiling point inversion was observed on passing from 1-methyl- to 1-ethyl-4-tert-butylcyclohexane [12]. Verkade and Van Bekkum and co-workers [13], in an examination of a number of limitations of the Auwers-Skita rule, proposed that the rule be used only for the refractive indexes and densities of isomers. All that has been set forth above is evidence in favor of the concept that the high-boiling isomers of 2,5-dialkyl-1,3-dioxanes, which have lower densities and refractive indices as well as dipole moments which are close to or even greater than 1.90D, are the trans isomers, which exist in the preferred chair conformation with a diequatorial orientation of the alkyl substituents. This conclusion is in agreement with the data of the PMR spectra which indicate a rigid chair conformation with the above-indicated substituent orientation [4].

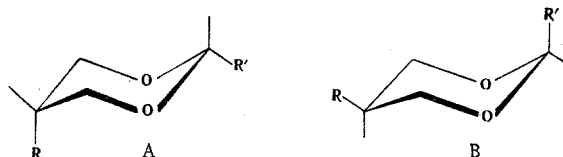
The situation is more complex with the low-boiling isomers. The low-boiling isomers have higher densities and refractive indices, which is evidence in favor of their cis configuration.

The NMR method leads to the same conclusion [4], but the problem of the conformation of such cis isomers is more complex. A study of the NMR spectra leads to the conclusion that the low-boiling isomers of I and II have a partially distorted symmetrical boat conformation; the low-boiling isomers of III and V have the chair conformation; the low-boiling isomers of IV and VI have the unsymmetrical boat conformation [4, 5]. The question of whether these data are in agreement with the results of DM measurements should be answered.

The DM of low-boiling isomer Ia was not measured; the DM of low-boiling isomer IIa is very close to the DM of the high-boiling isomer. In view of the possible distortions of the symmetrical boat conformation, which we previously noted in [4], it can be stated that this value does not contradict the symmetrical boat conformation.

At first glance, the symmetrical boat conformation is unlikely in view of the bow-stern interactions (the distance is  $\sim 1.8$  Å). However, the same NMR spectra indicate partial distortion of this boat to a conformation in which the  $\text{CH}_{\text{HS}}$  bond forms a dihedral angle of  $\Phi \sim 90^\circ$  with the two C-H bonds of the 4- $\text{CH}_2$  and 6- $\text{CH}_2$  groups, but forms a dihedral angle of  $\Phi \sim 0^\circ$  with the two other C-H bonds. This sort of conformation differs from the "ideal" twist form and approaches the chair conformation. It is easy to see that this sort of treatment of the problem under consideration does not contradict the DM data.

The DM of low-boiling isomers IIIa and Va are in complete agreement with the chair conformation, which follows from the NMR spectral data. Moreover, one can conceive of two chair conformations with an axial-equatorial orientation of the substituents, viz., A and B. Conformation A is undoubtedly the more preferred one, since its energy differs from the energy of the diequatorial conformation by only 0.81 kcal/mole [14], while the energy of conformation B is higher than the energy of the diequatorial conformation by  $\sim 2$  kcal/mole [15].



This also follows from previously published investigations [16] which indicate the advantageousness of placing a tert-butyl group in the 5-C-axial position, from our investigations [4, 17] in which the advantageousness of an analogous orientation of the isopropyl group was demonstrated, and also from recently published studies [14] devoted to an estimate, on the basis of a study of the NMR spectra, of the energy difference between the 5-C-axial and 5-C-equatorial conformations of 5-methyl-1,3-dioxane. Similar results are contained in [18, 19].

Consequently, from both the results of the DM method and from the NMR spectral data, the low-boiling isomers of III and V have a cis configuration, a chair conformation, and axial-equatorial orientation of the substituents.

There is a contradiction between the NMR and DM data in the estimate of the conformation of the low-boiling isomers of IV and VI and ketals VII-IX. According to the NMR spectral data, all of these compounds have a partially distorted, unsymmetrical boat conformation; according to the DM data, this conformation is unlikely. This contradiction is difficult to explain. A possible route to the explanation of this contradiction may be an estimate of the degree of distortion of the unsymmetrical boat conformation, which can invert to the chair conformation. In any case, the DM measurements attest to the definite probability of the DM values in the studied series of I-IX and do not give a clear picture of the change in the conformations of the low-boiling isomers as a function of the nature of the substituents.

## EXPERIMENTAL

The DM of 2,5-dialkyl-1,3-dioxanes were measured at  $25^\circ$  in benzene via the method in [20]. The Hedestrand method was used for extrapolation of the molar polarization. The atomic polarization was not taken into account, while the electronic polarization was taken as equal to the molecular refraction ( $\text{MR}_D$ ). The results of the DM measurements are presented in Table 1. Here,  $\epsilon_1$  and  $d_1$  are the dielectric permeability and solvent density determined by the method of least squares,  $\alpha$  and  $\beta$  are the coefficients in the Hedestrand equation, and  $P_{2\infty}$  is the polarization of the dissolved substance extrapolated to infinite dilution. The compounds used in the investigation were described in [4].

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