

CHROM. 11,629

Note

Application of gas chromatographic retention to the study of conformations of stereoisomers

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(First received August 2nd, 1978; revised manuscript received November 15th, 1978)

In a gas chromatographic (GC) study of stereoisomeric 1,3-dioxanes we observed large differences between the retention times of some pairs of stereoisomers, whereas other pairs display only a minimal difference when examined under the same experimental conditions; indeed, in certain cases they virtually cannot be separated chromatographically (see Table I).

The conformations of the tabulated compounds have been studied by means of various methods by Bogatskii *et al.*¹ They found that, as regards the pairs (1) and (2) and (3) and (4), there is no essential difference between the conformations of the individual stereoisomers: each is in the chair conformation (A)¹. In the case of the pairs (5) and (6) and (7) and (8), however, there is a difference between the conformations of the two isomers: (5) and (7) have chair conformations (A), whereas the structure of (6) or (8) is a deformed chair (B)². The deviation from the stable conformation A depends on the size of the substituents on the ring. The numerical values given in column 4 of Table I give a measure of this deviation. The greater the value of

$$\frac{T - C}{T + C} \cdot 100$$

the greater is the difference between the conformations of the two geometrical isomers.



The difference between the conformations of the isomers also appears in their solubilities, leading to different retentions. Our experimental data indicate that the difference between the retentions of the stereoisomers varies in direct proportion to the difference between the conformations of the individual isomers.

A similar tendency can be seen on the experimental data of Eliel and Knoeber³, which also provide the chance to deduce certain regularities in the relationship between conformational energy and retention time. (It should be noted that the configurations and probable conformations of the variously substituted 1,3-dioxane stereoisomers

TABLE I

GC RETENTION DATA ON STEREOISOMERIC 1,3-DIOXANES

GC column: 2 m 15% Carbowax 20 M/Kieselguhr + 2 m 15% Apiezon M Grease/Kieselguhr.
Temperature: 200°.

Compound	Structure	Retention time (min)	$\frac{T - C}{T + C} \cdot 100^*$	Conformation	Ref.
(1) <i>r</i> -2-Isopropyl- <i>cis</i> -5-ethyl-5-(2-methoxyethyl)-1,3-dioxane		18.8		A	
(2) <i>r</i> -2-Isopropyl- <i>trans</i> -5-ethyl-5-(2-methoxyethyl)-1,3-dioxane		20.0	3.1	A	1
(3) <i>r</i> -2-Methyl- <i>trans</i> -5-(2-ethoxyethyl)-5-isopropyl-1,3-dioxane		19.5		A	
(4) <i>r</i> -2-Methyl- <i>cis</i> -5-(2-ethoxyethyl)-5-isopropyl-1,3-dioxane		20.5	2.5	A	1
(5) <i>r</i> -2-Methyl- <i>cis</i> -5-ethyl-5-isopropoxymethyl-1,3-dioxane		7.0		A	
(6) <i>r</i> -2-Methyl- <i>trans</i> -5-ethyl-5-isopropoxymethyl-1,3-dioxane		8.6	10.3	B	2
(7) <i>r</i> -2-Isopropyl- <i>cis</i> -5-ethyl-5-isopropoxymethyl-1,3-dioxane		11.4		A	
(8) <i>r</i> -2-Isopropyl- <i>trans</i> -5-ethyl-5-isopropoxymethyl-1,3-dioxane		14.7	12.6	B	2

* T: retention time of isomer with *trans* configuration; C: retention time of isomer with *cis* configuration.

are well characterized, mainly as a result of work by Eliel *et al.*⁴ and Anteunis *et al.*⁵; Methods used include NMR spectroscopy, and the determination of equilibrium constants and conformational energies, the latter by means of the Lewis-acid-catalysed configurational isomerization of the stereoisomers.) However, as the various chromatographic procedures are also employed in the synthesis of the stereoisomers, useful information on the stereostructures of the individual isomers may be obtained even in the early stages of the work, by determination of the retention data on the stereoisomeric pairs under the same chromatographic conditions.

These results relate to the 1,3-dioxanes and to GC. However, there seems to be no reason why comparable results should not be obtained with other types of compound and other chromatographic methods.

ACKNOWLEDGEMENTS

I thank Prof. Bogatskii and his colleagues for providing the stereoisomeric 1,3-dioxanes.

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