в данных условиях нельзя добиться вполне стабильной нулевой линии. С повышением температуры скорость газа уменьшается (это надо учитывать и при количественных расчетах [2]), что также влияет на работу катарометра. Можно надеяться, что при работе с пламенно-ионизационным детектором этот недостаток будет устранен.

При анализе высококипящих соединений очень важное значение имеет стабильность неподвижной фазы. В наших опытах выяснилось, что улетучивание фаз начинается при следующих температурах: полиэтиленгликоль 4000 при 225°; полиэтиленгликоль 20 *M* при 240°; полипропиленгликольадипинат при 250°; апиезон *L* при 320°.

Описанное приспособление для программирования можно изготовить в любой механической мастерской. Его конструкция позволяет быстро переходить с программирования на изотермическую работу и при обоих режимах использовать одинаковые хроматографические колонки.

ЛИТЕРАТУРА

1. Leibnitz E., Struppe H. G., Handbuch der Gaschromatographie, Akademische Verlagsgesellschaft, Leipzig, 1966, S. 483.
2. Harris W. E., Habgood H. W., Programmed temperature gas chromatography, John Wiley and Sons, New-York, 1966, p. 209.

Институт химии
Академии наук Эстонской ССР

Поступила в редакцию
11/III 1968

EESTI NSV TEADUSTE AKADEEMIA TOIMETISED. XVII KÖIDE
KEEMIA * GEOLOOGIA. 1968, Nr. 3

ИЗВЕСТИЯ АКАДЕМИИ НАУК ЭСТОНСКОЙ ССР. ТОМ XVII
ХИМИЯ * ГЕОЛОГИЯ. 1968, № 3

E. LIPPMAA, T. PEHK

CARBON-13 CHEMICAL SHIFTS OF GEOMETRICAL (CIS-TRANS) ISOMERS

E. LIPPMAA, T. PEHK. SÜSINIK-13 KEEMILISED NIHKED GEOMEETRILISTES (CIS-TRANS) ISOMEERIDES

Э. ЛИППМАА, Т. ПЕХК. ХИМИЧЕСКИЕ СДВИГИ УГЛЕРОДА-13 В ГЕОМЕТРИЧЕСКИХ (ЦИС-ТРАНС) ИЗОМЕРАХ

Savitsky and Namikawa have shown that C^{13} chemical shifts of unsaturated carbon atoms in 1,2-disubstituted ethylene derivatives depend upon the geometrical configuration of these molecules [1]. Saturated carbon atoms appear to be even more susceptible. The chemical shifts of α-carbon atoms in all cis-trans pairs of normal alkenes differ by 5.7 ± 1 ppm and this difference depends neither on the type of the α-carbon atom (methyl or methylene) nor on the position of the double bond in the molecule [2,3]. This chemical shift, as compared with the chemical shift of corresponding carbon atoms in alkanes, is always diamagnetic in cis-isomers and paramagnetic in trans-isomers. Since the influence of polar groups on the carbon chemical shifts in aliphatic chains is also very regular [4], it is possible to predict these shifts with fair accuracy. The predicted and ex-

Table 1. **C^{13} chemical shifts δ_{CS_2} of oleic and elaidic acids, in ppm from external carbon disulfide**

Compound		C_1	C_2	C_3	C_{4-7}	C_8	$C_{9,10}$	C_{11}	C_{12-15}	C_{16}	C_{17}	C_{18}
Oleic acid (cis)	Exptl.	13.0	158.6	168.1	163.1	165.3	63.0	165.3	163.1	160.7	170.0	178.5
	Calcd.	12.5	159	168	163.5	166	63.5	166	163.5	161.5	170.5	179.5
	Δ	0.5	—0.4	0.1	—0.4	—0.7	—0.5	—0.7	—0.4	—0.8	—0.5	—1.0
Elaidic acid (trans)	Exptl.	12.9	160.6	168.7	163.6	161.1	63.3	161.1	163.6	161.1	170.4	179.2
	Calcd.	12.5	159	168	163.5	160.5	63.0	160.5	163.5	161.5	170.5	179.5
	Δ	0.4	1.6	0.7	0.1	0.6	0.3	0.6	0.1	—0.4	—0.1	—0.3
2-Hexenoic acid		C_1	C_2	C_3	C_4	C_5	C_6					
	Exptl.	21.3	72.8	41.9	159.2	172.3	180.1					

perimental chemical shifts of C^{13} in 9-cis octadecenoic (oleic) acid and 9-tnasoctadecenoic elaidic) acid are given in Table 1. The good fit between experimental and calculated values shows that C^{13} spectroscopy is a useful new tool for the study of geometrical isomerism about double bonds. Even conjugated substituents do not invalidate the results, the chemical shift of C_4 showing a particular unlabeled sample of 2-hexenoic acid (Th. Schuchardt, München) to be the more common trans isomer. The proton spectra of oleic and elaidic acids are also slightly different [5], but hopelessly complicated; the very small difference between the chemical shifts of α-methylene protons (0,08 ppm) is of little value, since proton shifts are quite susceptible to magnetic and solvent effects and the correlation with geometrical isomerism [16] is only partial, with many exceptions.

As it was pointed out by us [6], the nonbonded 1,4-interactions, well known in conformation studies with the use of other methods [18], have an important role in C^{13} spectra of alicyclic compounds and some substituted alkanes [4]. To get more data about this interaction, we investigated the C^{13} spectra of some disubstituted cyclohexanes and the isomers of decalin. The proton spectra of these compounds are rather featureless [7, 8, 11–15], and only some mean values for the chemical shifts of the ring protons can be measured. The dependence of proton screening upon orientation (axial or equatorial) complicates the problem still further. The total widths of methylene multiplets have been used for the determination of cis and trans isomers [8]. For detailed investigations of the proton spectra of these compounds much more sophisticated methods have to be used, among them preparation of various deuterated derivatives and the use of homonuclear double resonance [9, 10].

Among the cis-dimethylcyclohexanes the 1,2- and 1,4-isomers have e, a- (equatorial, axial) and 1,3-isomer e, e-conformation [18], while the reverse is true for the trans isomers. Differences of stabilities of the particular cis and trans isomers are semiquantitatively explained by nonbonded gauche interactions, the trans 1,2- or 1,4- and cis 1,3-isomers, where this sort of intramolecular interaction is less prevalent or absent, being the more stable ones. The thermodynamically less stable isomers provide many possibilities for the nonbonded 1,4-interaction and all carbon atoms in these compounds show diamagnetic shifts relative to the shifts of corresponding atoms in the more stable isomers. The experimental results show that all four atoms involved in the 1,4-gauche interaction are perturbed. The chemical shifts of unperturbed carbon atoms (all atoms of cis 1,3- and trans 1,4- isomers and C_{3-6} of trans 1,2- dimethylcyclohexane) are additive and can be calculated with excellent accuracy from the chemical shifts of cyclohexane and methyl cyclohexane [6].

All carbon chemical shifts were measured from absorption spectra, using frequency sweep and total decoupling of all hydrogen nuclei of the molecule [19]. This technique provides a high signal to noise ratio, is no more difficult to apply than monoresonance and allows to use frequency counters for exact and direct measurement of chemical shifts. The use of frequency sweep and a very strong perturbing field are the main differences between our technique and the method of Grant and Paul [17]. The spectral resolution and accuracy were both about 0.4 ppm. All data about disubstituted cyclohexanes are given in Table 2.

The nonbonded 1,4-interaction is clearly active in cyclohexanediols as well, leading to diamagnetic shifts in cis isomers. It is interesting to note that if one uses the arithmetic mean between chemical shifts of axial and equatorial protons, then the protons in the trans isomer are the more shielded ones [9].

Table 2. C^{13} **chemical shifts** δ_{CS_2} **in ppm of disubstituted cyclohexanes**

Compound	Carbon atoms of the ring						Side chain CH_3
	C_1	C_2	C_3	C_4	C_5	C_6	
1,2-cis Dimethylcyclohexane	158.7	158.7	161.5	169.3	169.3	161.5	177.0
1,2-trans Dimethylcyclohexane	153.5	153.5	157.2	166.1	166.1	157,2	172.6
1,3-cis Dimethylcyclohexane	159.6	147.9	159.6	157.5	166.3	157.5	169.7
1,3-trans Dimethylcyclohexane	165.7	151.5	165.7	159.0	171.6	159.0	172.1
1,4-cis Dimethylcyclohexane	162.1	161.4	161.4	162.1	161.4	161.4	172.2
1,4-trans Dimethylcyclohexane	159.5	156.6	156.6	159.5	156.6	156.6	169.5
1,2-cis Dihydroxy cyclohexane	122.9	122.9	164.0	172.0	172.0	164.0	—
1,2-trans Dihydroxy cyclohexane	118.0	118.0	160.2	168.8	168.8	160.2	—
1,4-cis Dihydroxy cyclohexane	126.4	163.7	163.7	126.4	163.7	163.7	—
1,4-trans Dihydroxy cyclohexane	124.5	161.0	161.0	124.5	161.0	161.0	—

Three 1,4-interactions in cis-decalin against nil in the trans isomer [18] probably constitute the main reason for diamagnetic chemical shifts in the former, the difference for C_9 and C_{10} extendig to 8 ppm (see Table 3).

Table 3. C^{13} **chemical shifts** δ_{CS_2} **in ppm of cis and trans decalin**

	$C_{1,4,5,8}$	$C_{2,3,6,7}$	$C_{9,10}$
cis Decalin	163.4	168.5	156.1
trans Decalin	158.2	165.7	148.8

It appears that NMR spectra of C^{13} can provide valuable information about molecular conformation and can be used as an absolute method for the determination of some cis and trans isomers without recourse to model compounds. The influence of other substituent groups is slight and predictable. Quantitative determination of isomer ratios is also possible.

Experimental

Dimethyl cyclohexanes were commercial products and happened to contain the particular cis and trans isomers in ratios that allowed for an easy assignment of spectral lines even without isomer separation. 1,2-dimethylcyclohexane (Fluka) and decalin (BDH) were also partly separated by column rectification. All mixtures of isomers were analysed by GLC, using a Shandon FB-4 gas chromatograph and columns with Tween-80 on Chromosorb W. The retention volumes of hydrocarbons on Tween-80 are given by Eisen et al. [20]. 1,2-cis Cyclohexanediol was a commercial product (Schuchardt), but the trans isomer was synthesized by the action of performic acid on cyclohexene [21]. The commercial mixture of cis and trans isomers of 1,4-cyclohexanediol (Schuchardt) was separated, through the use of different solubilities in cold acetone [22]. Elaidic acid was prepared by isomerisation of oleic acid with selenium [23].

REFERENCES

1. Savitsky G. B., Namikawa K., J. Phys. Chem., **67**, 2754 (1963).
2. Lippmaa E., Rang S., Eisen, O., Pehk, T., Изв. АН ЭССР, Хим. Геол., **16**, № 4, 351 (1967).
3. Ранг С., Липпмаа Э., Пехк Т., Эйзен О., Изв. АН ЭССР, Хим. Геол., **17**, № 3, 294 (1968).
4. Lippmaa E., Pehk T., Изв. АН ЭССР. Хим. Геол., **17**, № 3, 210 (1968).
5. Purcell J. M., Morris S. G., Susi H., Anal. Chem., **38**, 588 (1966).
6. Пехк Т., Липпмаа Э., Изв. АН ЭССР. Хим. Геол., **17**, № 3, 291 (1968).
7. Bacskai R., J. Polymer Sci., A1, 2788 (1963).
8. Brownstein S., Miller R., J. Org. Chem., **24**, 1886 (1959).
9. Trager W. F., Nist B. J., Huitric A. C., Tetrahedron Lett., 267 (1965).
10. Lemieux R. U., Lown J. W., Can. J. Chem., **42**, 893 (1964).
11. Musher J. J., Spectrochim. Acta, **16**, 835 (1960).
12. Самитов Ю. Ю., Некоторые вопросы органической химии, Изд. Казанского ун-та, 1965, с. 182.
13. Clarke R. L., J. Am. Chem. Soc., **83**, 965 (1961).
14. Monitz W. B., Dixon J. A., J. Am. Chem. Soc., **83**, 1671 (1961).
15. Muller N., Tosch W. C., J. Chem. Phys., **37**, 1167 (1962).
16. Stehling F. C., Bartz K. W., Anal. Chem., **38**, 1467 (1966).
17. Paul E. G., Grant D. M., J. Am. Chem. Soc., **86**, 2977, 2984 (1964).
18. Eliel E. L., Stereochemistry of carbon compounds, McGraw-Hill, 1962.
19. Lippmaa E., Pehk T., Past J., Изв. АН ЭССР, Физ. Матем., **16**, № 3, 345 (1967).

Изв. АН ЭССР, Физ.-матем. **16**, № 3, 345 (1967).

20. Эйзен Ю., Киррет О., Эйзен О., Изв. АН ЭССР, Сер. физ.-матем. и техн. наук, **13**, № 1, 22 (1964).
21. Синтезы органических препаратов, ред. А. Ф. Платэ, сб. 4, ИЛ, 1953, с. 559.
22. Palfray L., Rothstein L., Compt. Rend., **186**, 873 (1928).
23. Biochemical Preparations, ed. E. Snell, **3**, 118 (1953).

Note added in proof: D. K. Dalling and D. M. Grant [J. Am. Chem. Soc., **89**, 6612 (1967)] have recently published carbon shieldings for methylcyclohexanes.

Academy of Sciences of the Estonian SSR,
Institute of Cybernetics

Received
April 9, 1968