CAPILLARY GAS–LIQUID CHROMATOGRAPHY OF PYRIDINE ALKYL HOMOLOGUES

Marta Novrocíková, Jan Novrocík and Jan Vyměтal

Research Institute of Coal Tar Chemistry, Urx Works, 757 27 Valašské Meziříčí

Received August 31st, 1982

The Kováts retention indices (*I*) were determined by capillary gas–liquid chromatography on three stationary phases of different polarity, *viz.* OV-1, Ucon LB-550, and Reoplex 400, for 70 pyridine alkyl homologues present in coal tar. The increments for some alkyl groups were assessed, and the Kováts indices were predicted for 46 pyridine alkyl homologues and compared with the experimental data. The parameters of the linear dependences $I_{(1)} = kI_{(2)} + q$ for pairs of stationary phases (*1*) and (*2*) were evaluated.

Alkyl homologues of pyridine are conveniently identified by gas–liquid chromatographic treatment on packed columns or on capillary columns, which have become widespread over the past 15 years. A review of this topic has been presented by Nabivach and Venger[1], who have concerned themselves particularly with the factors affecting the analysis of pyridine and quinoline bases, the use of reaction chromatography, and the analysis of such substances in industrial mixtures. Pyridine bases have been analyzed by capillary gas–liquid chromatography (GLC) in glass capillary columns wetted with Carbowax 20M (ref.[2]), Carbowax 1540 (ref.[2]), polypropyleneimine[3], polyethyleneimine[3], N,N-bishydroxyethyltrimethyldiamine[4], PEG 20 000 (ref.[5]), silicon GE SF-96 (ref.[6]), Igepal CO 880 (ref.[6]), methylsiloxane[7], Amin 220 (refs[8,9]), Reoplex 400 (ref.[8]), PEG 400 (ref.[8]), Apiezon H (ref.[8]), and PEG 40M (ref.[10]). Stainless steel capillary columns wetted with d-sorbitol combined with nickel dichloride[11], SE-30 (ref.[12]), or Amin 220 (refs[12,13]) have also been employed. In order to suppress peak tailing, potassium hydroxide has occasionally been added to the stationary phase solution prior to its application[2,5,8,12].

The present work is devoted to the study of the numerous series of pyridine alkyl homologues present in coal tar from the points of view of their identification by capillary GLC on phases of different polarity and of their retention behaviour, which is a problem that so far has not received due attention.

EXPERIMENTAL

The pyridine alkyl homologues, isolated from coal tar and identified by classical and spectral methods (NMR, GLC–MS, IR), were analyzed by capillary GLC on a Fractovap 4160 instrument (Carlo Erba, Milan) fitted with an inlet splitter (set to a value of 1 : 100), a flame ionization detector, and a temperature programmer. The column parameters were as given in Table I. The column with OV-1 silicone phase was a commercial product of Carlo Erba, Milan, columns 2—4

were prepared as follows: the inner surface of the capillary columns made of Unihost sodium-calcium glass (Sklo-Union, Hostomice) was roughened by etching with methyl 1,1,2-trifluoro-chlorethyl ether at 350°C. After purging with argon, the capillary was wetted dynamically by the mercury plug method[14] using an approximately 20% solution of the stationary phase of interest in benzene. The columns prepared were stabilized thermally at 130 C, and their efficiency was tested. Analyzed were approximately 5% solutions of pyridine alkyl homologues in benzene at 70°C; the argon flow rate through columns 1—4 was 0·5, 1·0, 1·0, and 1·1 ml min^{-1}, respectively. The dead volume of the columns was determined by using methane under the same chromatographic conditions. The Kováts indices for the pyridine alkyl homologues derived from the experimental data were determined as averages of triplicate measurements. The parameters were also evaluated of the linear relations $I_{(1)} = kI_{(2)} + q$, where $I_{(1)}$ and $I_{(2)}$ are the retention indices on a less polar stationary phase (1) and on a more polar stationary phase (2), respectively.

RESULTS AND DISCUSSION

The experimental data confirm that capillary GLC on columns wetted with stationary phases of different polarity constitutes a sufficiently efficient technique for the identification of pyridine alkyl homologues present in coal tar. As indicated by the data of the separation efficiency (Table I) and of the Kováts indices (Table II), the analyzed and previously identified pyridine alkyl homologues separated best on the column wetted with Reoplex 400, whose overall efficiency was approximately 114 000 theoretical plates; only three pairs and a triad of substances remained unresolved. The peaks of all of the pyridine alkyl homologues as well as of pyridine itself were symmetrical although no potassium hydroxide had been added to the stationary phase solution. This fact can be accounted for in terms of the material of the capillary: the soft sodium-calcium glass contained a sufficient amount of alkali (17.8% (m/m) sodium oxide, 1.3% (m/m) potassium oxide, and 5·5% (m/m) calcium oxide), although part of it had obviously been neutralized by hydrogen chloride or fluoride produced

TABLE I
Parameters of the capillary columns used

Column No	Stationary phase	Column length m	Inner diameter mm	n^a	k^b
1	OV-1 (Carlo Erba, Milan)	25	0·25	60 000	4·5
2	Ucon LB-550 (Appl. Sci., USA)	45	0·26	94 300	8·0
3	Reoplex 400 (Appl. Sci., USA)	45	0·26	114 200	4·3
4	Ucon LB-550 + 5% Marlazin L10 (Chem. Werke Hülls, FRG)	45	0·26	95 400	7·8

[a] Number of theoretical plates; [b] capacity ratio with respect to 1,2,4,5-tetramethylbenzene.

TABLE II

Experimental and calculated Kováts indices (I) of pyridine alkyl homologues

Alkyl substitution	Kováts indices for the stationary phases					
	OV-1		Ucon LB-550		Reoplex 400	
	I_{exp}	I_{calc}	I_{exp}	I_{calc}	I_{exp}	I_{calc}
—	757·6	—	899·2	—	1 182·2	—
2-Methyl	815·3	—	956·5	—	1 217·8	—
3-Methyl	857·2	—	1 011·5	—	1 290·8	—
4-Methyl	857·2	—	1 015·1	—	1 297·3	—
2,6-Dimethyl	877·5	873·0	1 011·5	1 013·8	1 261·4	1 253·4
2-Ethyl	897·1	—	1 032·0	—	1 276·3	—
2,5-Dimethyl	921·3	914·9	1 064·4	1 068·8	1 320·8	1 326·4
2,4-Dimethyl	921·3	914·9	1 070·6	1 072·4	1 331·1	1 332·9
2,3-Dimethyl	933·3	—	1 082·0	—	1 351·8	—
3-Ethyl	945·0	—	1 094·8	—	1 367·3	—
4-Ethyl	951·7	—	1 102·2	—	1 380·9	—
2-Ethyl-6-methyl	955·2	954·8	1 073·0	1 089·3	1 296·1	1 311·9
3,5-Dimethyl	963·1	956·8	1 121·4	1 123·8	1 398·5	1 399·4
2,4,6-Trimethyl	980·4	977·1	1 121·4	1 127·4	1 363·6	1 376·5
3,4-Dimethyl	980·4	—	1 152·0	—	1 446·8	—
2-Propyl	983·7	—	1 112·9	—	1 349·1	—
2,3,6-Trimethyl	994·5	990·7	1 129·5	1 139·3	1 376·2	1 387·4
2-Ethyl-4-methyl	1 001·8	996·7	1 138·4	1 147·9	1 385·5	1 391·4
2-Ethyl-5-methyl	1 003·3	996·7	1 136·5	1 144·3	1 380·9	1 384·9
5-Ethyl-2-methyl	1 009·3	1 010·9	1 143·9	1 152·1	1 398·5	1 402·9
4-Ethyl-2-methyl	1 012·0	1 009·4	1 158·0	1 159·5	1 412·1	1 416·5
4-Isopropyl	1 012·0	—	1 158·0	—	1 421·2	—
3-Propyl	1 031·6	—	1 180·8	—	1 460·1	—
2-Methyl-6-propyl	1 035·6	1 041·3	1 152·0	1 170·2	1 364·4	1 384·7
4-Propyl	1 037·8	—	1 188·9	—	1 452·0	—
2,3,5-Trimethyl	1 037·8	1 032·9	1 191·9	1 194·3	1 454·7	1 460·4
2,4,5-Trimethyl	1 046·3	1 038·1	1 208·0	1 209·3	1 477·5	1 482·4
3-Ethyl-5-methyl	1 049·4	1 044·6	1 206·2	1 207·1	1 472·7	1 475·9
2-Ethyl-4,6-dimethyl	1 051·8	1 059·5	1 180·8	1 195·7	1 401·6	1 421·1
2,3,4-Trimethyl	1 061·9	1 056·5	1 125·5	1 225·5	1 405·7	1 507·8
2-Ethyl-3,6-dimethyl	1 067·1	1 073·2	1 193·2	1 198·5	1 419·4	1 430·1
4-Ethyl-2,6-dimethyl	1 067·1	1 069·7	1 208·0	1 215·3	1 440·6	1 447·7
4-Ethyl-3-methyl	1 070·8	—	1 236·5	—	1 520·6	—
4-tert-Butyl	1 070·8	—	1 218·0	—	1 477·5	—
3-Ethyl-2,6-dimethyl	1 074·3	1 074·4	1 209·1	1 216·0	1 445·5	1 462·5
4-Methyl-2-propyl	1 082·1	1 083·2	1 221·3	1 228·8	1 452·8	1 464·2
Cyclopenteno(*b*)	1 082·1	—	1 257·6	—	1 557·9	—

TABLE II
(*Continued*)

Alkyl substitution	Kováts indices for the stationary phases					
	OV-1		Ucon LB-550		Reoplex 400	
	I_{exp}	I_{calc}	I_{exp}	I_{calc}	I_{calc}	I_{exp}
5-Methyl-2-propyl	1 084·4	1 083·2	1 220·1	1 225·2	1 451·3	1 457·7
2,5-Diethyl	1 086·4	1 084·5	1 222·9	1 227·6	1 454·7	1 461·4
2-Methyl-5-propyl	1 094·0	1 089·3	1 236·5	1 238·1	1 472·7	1 495·7
2-Methyl-4-propyl	1 096·0	1 095·5	1 240·8	1 246·2	1 481·1	1 487·6
3,5-Diethyl	1 099·0	1 132·4	1 256·0	1 290·4	1 523·0	1 552·4
2-Ethyl-6-propyl	1 104·5	1 123·1	1 209·1	1 245·7	1 395·8	1 443·2
2-Isopropyl-3,6-dimethyl	1 104·5	—	1 214·3	—	1 414·3	—
2,3,5,6-Tetramethyl	1 104·5	1 109·0	1 251·3	1 264·8	1 500·4	1 521·4
2-Ethyl-3,5-dimethyl	1 106·7	1 102·6	1 250·4	1 254·2	1 495·2	1 492·6
7-Methylcyclopenteno(*b*)	1 109·7	—	1 263·3	—	1 532·5	—
3-Methylthio	1 109·7	—	1 335·0	—	> 1 700	—
3,4,5-Trimethyl	1 113·8	1 103·6	1 297·4	1 288·9	1 599·3	1 596·3
2,3,4,6-Tetramethyl	1 116·7	1 117·7	1 271·5	1 270·0	1 529·2	1 516·7
2-Methylcyclopenteno(*b*)	1 118·4	—	1 268·2	—	1 520·9	—
Cyclopenteno(*c*)	1 119·3	—	1 303·3	—	1 612·4	—
2,6-Diethyl-4-methyl	1 122·0	1 136·2	1 236·5	1 222·1	1 434·7	1 406·0
3-Ethyl-2,5(5,6)-dimethyl	1 123·9	1 120·7[a]	1 276·3	1 277·7[a]	1 529·2	1 536·9[a]
3-Isopropyl-4-methyl	1 123·9	—	1 282·2	—	1 555·0	—
2-Ethyl-4,5-dimethyl	1 124·8	1 119·9	1 277·0	1 284·8	1 529·9	1 540·9
5-Ethyl-2,4-dimethyl	1 124·8	1 118·2	1 283·4	1 275·1	1 544·3	1 532·2
2-Butyl-6-methyl	1 127·6	—	1 229·1	—	1 425·0	—
4-Ethyl-2,5-dimethyl	1 132·6	1 134·9	1 282·2	1 289·4	1 544·3	1 550·6
4-Ethyl-2,3-dimethyl	1 132·6	1 146·9	1 187·4	1 307·0	1 447·0	1 581·6
2,4-Diethyl-6-methyl	1 139·9	1 149·3	1 261·8	1 276·0	1 472·7	1 494·8
3,4-Diethyl	1 148·6	—	1 306·7	—	1 582·0	—
4-Methylcyclopenteno(*b*)	1 148·6	—	1 212·9	—	1 593·6	—
4-Methyl-3-propyl	1 149·9	1 154·8	1 306·7	1 321·3	1 588·8	1 616·1
2,3(2,5)-Dimethyl-6-propyl	1 151·0	1 147·3[b]	1 272·5	1 278·1[b]	1 485·1	1 487·7[b]
2-Butyl-3,6(5,6)-dimethyl	1 151·0	—	1 270·9	—	1 486·4	—
2,6-Dimethyl-4-propyl	1 159·4	1 157·4	1 287·4	1 301·2	1 505·7	1 531·2
3-Ethyl-2,4,6-trimethyl	1 193·3	1 177·3	1 326·8	1 325·9	1 568·1	1 564·7
4-Ethyl-2,3,6-trimethyl	1 196·9	1 208·1	1 330·4	1 354·5	1 568·1	1 606·0
2-Ethyl-3(5),4,6-trimethyl	1 198·5	1 185·8[c]	1 330·4	1 340·8[c]	1 568·1	1 571·0[c]
2,4,6-Triethyl	1 211·9	1 230·7	1 311·4	1 367·8	1 498·5	1 569·1
2,6-Diethyl-3,4-dimethyl	1 256·7	1 259·4	1 369·0	1 417·6	1 586·3	1 635·0

For the more likely structure of [a] 3-ethyl-5,6-dimethylpyridine; [b] 2,5-dimethyl-6-propylpyridine; [c] 2-ethyl-3,4,6-trimethylpyridine.

by pyrolysis of methyl 1,1,2-trifluorochloroethyl ether used as the etching agent. No improvement of the separation efficiency or peak symmetry resulted if Marlazine L10 was added in a 5% quantity to the Ucon LB-550 phase. As it seems, the major factor determining the peak symmetry is the glass of which the capillary column has been made.

The separation of the pyridine alkyl homologues becomes poorer if a stationary phase exhibiting a lower efficiency, and also a lower selectivity, is used. On the column with Ucon LB-550, eight pairs of substances remained unresolved, and the column wetted with OV-1 stationary phase, displaying a low number of theoretical plates and a low selectivity, appeared to be unsuitable altogether: 14 pairs of compounds remained unresolved, among them substances of technological importance such as

TABLE III

Increments for the alkyl groups in pyridine alkyl homologues

Alkyl group	Position	Increment formula	Increment value		
			a	*b*	*c*
Methyl	2	$I_{2\text{-MePy}} - I_{\text{Py}}$	57·7	57·3	35·6
	3	$I_{3\text{-MePy}} - I_{\text{Py}}$	99·6	112·3	108·6
	4	$I_{4\text{-MePy}} - I_{\text{Py}}$	99·6	115·9	115·1
Ethyl	2	$I_{2\text{-EtPy}} - I_{\text{Py}}$	139·5	132·8	94·8
	3	$I_{3\text{-EtPy}} - I_{\text{Py}}$	187·4	195·6	185·1
	4	$I_{4\text{-EtPy}} - I_{\text{Py}}$	194·1	203·0	198·7
Propyl	2	$I_{2\text{-PrPy}} - I_{\text{Py}}$	226·0	213·7	166·9
	3	$I_{3\text{-PrPy}} - I_{\text{Py}}$	274·0	281·6	277·9
	4	$I_{4\text{-PrPy}} - I_{\text{Py}}$	280·2	289·7	269·8
Methyl[d]	2	$I_{2,3\text{-diMePy}} - I_{3\text{-MePy}}$	76·1	70·5	61·0
	3	$I_{2,3\text{-diMePy}} - I_{2\text{-MePy}}$	118·0	125·5	134·0
	4	$I_{3,4\text{-diMePy}} - I_{3\text{-MePy}}$	132·2	140·5	156·0
Methyl[d]	3	$I_{3,4\text{-diMePy}} - I_{4\text{-MePy}}$	132·2	136·9	149·5
Methyl[e]	4	$I_{3,4,5\text{-triMePy}} - I_{3,5\text{-diMePy}}$	150·7	176·0	200·8
Methyl[e]	3	$I_{2,3,4\text{-triMePy}} - I_{2,4\text{-diMePy}}$	140·6	54·9	74·6
Ethyl[f]	3	$I_{3,4\text{-diEtPy}} - I_{4\text{-EtPy}}$	196·9	204·5	201·1
	4	$I_{3,4\text{-diEtPy}} - I_{3\text{-EtPy}}$	203·6	211·9	214·7
Ethyl[d]	4	$I_{3\text{-Me-4-EtPy}} - I_{3\text{-MePy}}$	213·6	225·0	229·8

[a] For OV-1 stationary phase; [b] for Ucon LB-550; [c] for Reoplex 400; [d] with allowance for the presence of a methyl group in the *ortho* position; [e] with allowance for the presence of methyl groups in the two ortho positions: [f] with allowance for the presence of an ethyl group in the *ortho* position.

3- and 4-methylpyridine, 2,4- and 2,5-dimethylpyridine, 2,4,6-trimethylpyridine and 3,4-dimethylpyridine, and 2,3,5-trimethylpyridine and 4-propylpyridine. The retention data obtained on this nonpolar phase, however, can be of utility for estimating the order of pyridine alkyl homologues with respect to their boiling points.

An attempt was also made to estimate the Kováts indices based on the increments for some alkyl groups (methyl, ethyl, propyl), obtained as the differences of the experimental retention indices for the pyridine alkyl homologue and pyridine itself, or as some other suitable differences (Table III). The increments for alkyl groups in position 2 with respect to those in positions 3 and 4 are found to be considerably lower on the polar Reoplex 400 than on the medium polar or nonpolar stationary phases. This difference between the increments decreases with increasing length of the alkyl chain. This can be explained so that the alkyl group in position 2 suppresses considerably the polar interaction between solute and the polar stationary phase, and this effect diminishes with increasing molecular mass of the alkylpyridine, hence with increasing length of the alkyl chain. On all the stationary phases the increments are

TABLE IV

Formulae for the calculation of some Kováts indices

Alkyl substitution	Formula
2,4,6-Trimethyl	$I_{2,6\text{-diMePy}} + \Delta I_{4\text{-Me}}$
2,3,6-Trimethyl	$I_{2,3\text{-diMePy}} + \Delta I_{2\text{-Me}}$
2,3,5-Trimethyl	$I_{2,3\text{-diMePy}} + \Delta I_{3\text{-Me}}$
2,4,5-Trimethyl	$I_{3,4\text{-diMePy}} + \Delta I_{2\text{-Me}}$
2-Ethyl-4,6-dimethyl	$I_{2\text{-Et-4-MePy}} + \Delta I_{2\text{-Me}}$
2,3,4-Trimethyl	$I_{2,3\text{-EtMePy}} + \Delta I_{4\text{-Me}}$
2-Ethyl-3,6-dimethyl	$I_{2\text{-Me-6-EtPy}} + \Delta I_{3\text{-Me}}$
4-Ethyl-2,6-dimethyl	$I_{2\text{-Me-4-EtPy}} + \Delta I_{2\text{-Me}}$
2,3,5,6-Tetramethyl	$I_{\text{Py}} + 2(I_{2,3\text{-diMePy}} - \Delta I_{\text{Py}})$
2-Ethyl-3,5-dimethyl	$I_{3,5\text{-diMePy}} + \Delta I_{2\text{-Et}}$
3,4,5-Trimethyl	$I_{3,4\text{-diMePy}} + \Delta I_{3\text{-Me(corr)}}$
2,3,4,6-Tetramethyl	$I_{2,3,6\text{-triMePy}} + \Delta I_{4\text{-Me}}$
2,6-Diethyl-4-methyl	$I_{\text{Py}} + 2\Delta I_{2\text{-Et}} + \Delta I_{4\text{-Me}}$
3-Ethyl-5,6-dimethyl	$I_{2,3\text{-diMePy}} + \Delta I_{3\text{-Et}}$
4-Ethyl-2,5-dimethyl	$I_{2,5\text{-diMePy}} + \Delta I_{4\text{-Et(corr)}}$
4-Ethyl-2,3-dimethyl	$I_{4\text{-Et-3-MePy}} + \Delta I_{2\text{-Me(corr)}}$
2,4-Diethyl-6-methyl	$I_{2\text{-Et-6-Me}} + \Delta I_{4\text{-Et}}$
2,5-Dimethyl-6-propyl	$I_{2,5\text{-diMePy}} + \Delta I_{2\text{-Pr}}$
4-Ethyl-2,3,6-trimethyl	$I_{2,3,6\text{-triMePy}} + \Delta I_{4\text{-Et(corr)}}$
2-Ethyl-3,4,6-trimethyl	$I_{2,4,5\text{-triMePy}} + \Delta I_{2\text{-Et(corr)}}$
2,6-Diethyl-3,4-dimethyl	$I_{3,4\text{-diMePy}} + 2\Delta I_{2\text{-Et(corr)}}$

appreciably higher if an adjacent alkyl group is present, and this effect is still more pronounced if both adjacent positions are occupied. Thus, the mutual influencing of adjacent alkyl groups has to be allowed for when estimating the Kováts retention indices in this manner. The calculated retention indices are given in Table II for 46 pyridine alkyl homologues. Some retention indices were not calculated, either because their experimental values served as the basis for the evaulation of the increments (*e.g.*, 2,3- a,d 3,4-dimethylpyridine), or because the increments of the corresponding alkyl groups (2-butyl, 2- and 3-isopropyl) are unknown due to a lack of standards. The predicted Kováts indices agreed with the experimental data (determined with a precision of ± 3 retention units) to within ± 10 retention units in 85% cases on the nonpolar stationary phase, in 63% cases on the medium polar phase, and only in 48% cases on the polar phase. The calculated data for homologues with a higher

TABLE V

Parameters of the linear dependences $I_{(1)} = kI_{(2)} + q$ (with the correlation coefficients r) for stationary phase pairs (1)—(2)

Substitution	Parameters for the stationary phase pairs								
	OV-1 (1) — Ucon LB (2)			OV-1 (1) — Reoplex (2)			Ucon (1) — Reoplex (2)		
	k	$-q$	r	k	$-q$	r	k	$-q$	r
2-	1·0770	214·70	0·9999	1·2795	740·41	0·9989	1·1881	488·21	0·9991
3-	1·0301	184·06	0·9999	1·0262	464·05	0·9982	0·9967	272·48	0·9989
4-	1·0477	204·73	0·9995	1·1907	687·94	0·9984	1·1365	461·23	0·9989
2,3-	0·9141	56·07	0·9930	0·8158	166·28	0·9666	0·9078	143·27	0·9901
2,4-	1·0277	175·48	0·9976	0·8183	577·56	0·9805	1·1609	473·95	0·9955
2,5-	1·0078	146·74	0·9981	1·1773	630·59	0·9943	1·1685	480·53	0·9965
2,6-	1·1344	267·40	0·9994	1·5325	48·18	0·9926	1·2643	564·78	0·9976
3,5-	1·0137	173·60	0·9999	1·1136	593·25	0·9994	1·0998	415·85	0·9995
3,4-	1·0411	217·70	0·9873	1·0032	457·08	0·9293	0·9984	283·90	0·9753
2,3,4-	1·0193	83·56	[a]	1·7090	341·24	[a]	1·4969	28·39	[a]
2,3,5-	0·9427	212·45	0·9935	1·1731	662·00	0·9602	1·1428	466·71	0·9858
2,3,6-	1·0155	147·08	0·9720	0·7514	627·35	0·8209	0·8912	360·17	0·9319
2,4,5-	1·1096	293·94	0·9954	1·2604	813·72	0·9824	1·1392	473·46	0·9899
2,4,6	1·1693	333·14	0·9921	1·4065	928·21	0·9405	1·2369	558·12	0·9750
2,3,4,6-	1·4277	700·10	0·9993	2·3393	466·11	0·9852	1·6457	248·14	0·9903
3,4[b]	0·9124	258·02	0·9999	0·8078	654·31	0·9968	0·8856	425·60	0·9972
2,3,6-[c]	0·8930	241·24	0·9907	0·6665	711·04	0·9733	0·7771	493·67	0·9598

[a] Relation determined based on two points; [b] cyclopenteno(*c*)pyridine omitted; [c] 7-methylcyclopenteno(*b*)pyridine omitted.

number of alkyl groups disagreed with those derived from the experiment on all of the stationary phases: hence, the increments determined from the retention indices of homologues containing a lower number of alkyl groups fail to allow for the mutual interaction of all the alkyl groups, along with the heterocyclically bonded nitrogen, in the molecule of a higher substituted alkylpyridine.

Althouth an accuracy of the retention index estimate of ± 10 retention units is usually insufficient for an unambiguous indentification, the retention data obtained on the little selective and relatively least efficient column, *viz.* that wetted with OV-1 stationary phase, can be of utility for a prediction of the retention indices of most pyridine alkyl homologues. The formulae used for the calculation of the retention indices are given in Table IV. For cyclopenteno(*c*) pyridine the difference between the retention indices on the polar (or medium polar) stationary phase is higher than for the structurally related 4-ethyl-3-methylpyridine. Obviously, the overall polarity of the molecule is more increased by the cycloaliphatic ring than by the substituents in the latter substance. For cyclopenteno(*c*)-pyridine such a comparison could not be made because 2-ethyl-3-methylpyridine was unavailable. The retention order of the cyclopenteno- and methylcyclopentenopyridines is identical with that of the corresponding di- and trialkylpyridines.

The estimate of the retention indices based on the increments can be of assistance when assessing the mutual position of the alkyl groups in some alkylpyridines. For instance, of the possible alternatives of 3-ethyl-2,5-dimethylpyridine or 5-ethyl-2,3-dimethylpyridine the latter appears to be the more likely as its calculated indices approach the experimental values better than those of the former substance (Table IV). On this ground, of the pairs of 2,5-dimethyl-6-propylpyridine-2,3-dimethyl-6-propylpyridine and 2-ethyl-3,4,6-trimethylpyridine-2-ethyl-4,5,6-trimethylpyridine, always the former structure is given preference.

The parameters of the linear dependences $I_{(1)} = kI_{(2)} + q$ for stationary phase pairs (1)–(2), including the correlation coefficients, are given in Table V. The correlation coefficient becomes poorer if cyclopenteno(*c*)pyridine is included in the series of 3,4-dialkylsubstituted pyridines; this again documents that the presence of a cycloaliphatic ring brings about changes in the polarity of the molecule different from those induced by alkyl groups in positions 3 and 4. This applies also to 7-methylcyclopenteno(*c*)pyridine considered as a member of the 2,3,6-trialkylpyridine series. As follows from the data of Table V, the polarity decreases in the following orders of substitution: monoalkylpyridines: 3- > 4- > 2-; dialkylpyridines: 2,3- > 2,4- > > 3,4- > 3,5- > 2,5- > 2,6-; trialkylpyridines: 2,3,6- > 2,3,5- > 2,4,5- > 2,4,6- > > 2,3,4-. Other patterns (3,4,5- or 2,3,5,6-) could not be treated because of lack of the corresponding standards.

REFERENCES

1. Nabivach V. M., Venger L. N.: Zh. Anal. Khim. *30*, 604 (1975).
2. Cieplinski E. W.: Anal. Chem. *38*, 928 (1966).
3. Grob K.: J. Gas Chromatogr. *2*, 80 (1964).
4. Heyns K., Stube R., Winkler J.: J. Chromatogr. *21*, 302 (1966).
5. Pichler H., Hennenberger P., Schwarz Y.: Brennst. – Chem. *49*, 175 (1968).
6. Durbin D. E., Zlatkis A.: J. Chromatogr. Sci. *8*, 608 (1970).
7. Ilkova E. L., Mistryukov E. A.: Chromatographia *4*, 77 (1971).
8. Tesařík K., Ghyczy S.: J. Chromatogr. *91*, 723 (1974).
9. Kavan I., Tesařík K.: Ropa Uhlie *19*, 29 (1977).
10. Golovnya R. V., Mistryukov E. A., Samusenko A. L.: Izv. Akad. Nauk SSSR, Ser. Khim. *1977*, 1632; Chem. Abstr. *89*, 70 475.
11. Leddet M., Cuzin D., Coussemant F.: J. Chromatogr. *117*, 1 (1976).
12. Buryan P., Macák J., Lelek J.: Chem. Prům. *28*, 70 (1978).
13. Macák J., Nabivach V. M., Buryan P., Berlizov J. S.: J. Chromatogr. *209*, 472 (1981).
14. Onuska F. I., Afghan B. K., Wilkinson R. J.: J. Chromatogr. *158*, 23 (1978).

Translated by P. Adámek.