

CAPILLARY GAS CHROMATOGRAPHY OF TRIMETHYL- AND METHYLETHYLBIPHENYLS

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Capillary gas-liquid chromatography with three columns impregnated with non-polar, medium and polar stationary phases has been used for determination of the Kováts indexes of methyl-ethyl- and trimethylbiphenyls carrying the alkyl groups in the both rings. From elution data of isomeric methyl- and ethylbiphenyls the increments of methyl and ethyl groups have been determined, the theoretical Kováts indexes of the mentioned methylethyl- and trimethylbiphenyls have been calculated, and possibility of prediction and assessment of the Kováts indexes of these substances has been discussed. Parameters of the straight line given by the relation $I_{A_{\text{Piez.L}}} = k \cdot I_{\text{stat.phase}(2)} + q$ have been determined, and correlation coefficients of these relations have been estimated.

The papers by Adams¹ and Johnson² deal with identification of biphenyl and its methyl homologues in various mixtures of aromatic hydrocarbons from crude oil or other sources. The identification made use of spectral properties of these compounds. Another study by Johnson³ deals with UV spectral properties of dimethylbiphenyls prepared synthetically. Development of capillary gas-liquid chromatography (GLC) enabled closer identification of biphenyl and methylbiphenyls in mixtures with other hydrocarbons⁴⁻⁶. Pichler and coworkers⁷ used this method for identification of 3,3'- and 4,4'-dimethylbiphenyls in coal tar distillation cuts. Behaviour of these and other dimethyl-, ethyl- and isopropylbiphenyls during the capillary GLC is dealt with in ref.⁸. Further works^{9,10} describe isolation of di-, tri- and tetramethylbiphenyls from aromatic fractions of light gas oil from crude oil. The mentioned compounds were isolated by a combination of column chromatography, azeotropic rectification and preparative GLC and were identified by IR, UV and NMR spectroscopy.

From the mentioned literature sources it follows that alkylbiphenyls $C_{15}H_{16}$ can be encountered in some products of chemical or physical treatment of crude oil or coal. However, none of the available papers published so far deals with the capillary GLC of these compounds. The present communication describes in detail the chromatographic behaviour of the above-mentioned compounds prepared synthetically, the capillary columns used being impregnated with stationary phases of various polarity. The results could be useful for more complete identification of methylethylbiphenyls and trimethylbiphenyls in the above-mentioned industrial products.

EXPERIMENTAL

The used trimethyl- and methylethylbiphenyls were prepared by the Gomberg reaction and purified by column chromatography according to ref.¹¹. The same procedure was used for preparation of methyl-, ethyl- and dimethylbiphenyls necessary for comparison. The products were analyzed with the use of capillary columns (Table I) incorporated in a gas chromatograph Fractovap 2400T (Carlo Erba, Milano) equipped with a flame ionization detector and an inlet splitter. Further conditions of the analyses: $t_c = 170^\circ\text{C}$, the argon flow rate in the columns 1 to 3 was 0.35, 1.1 and 0.55 ml min⁻¹, respectively, the separation ratio at the inlet splitter was 1 : 100, feed 0.025 μl . The dead volume of each column at the mentioned conditions was established with methane feed. Under the same conditions, mixtures of C₁₄ to C₂₄ paraffins were analyzed in each column. The Kováts indexes were calculated from the results of three measurements in each case. The increments of methyl and ethyl groups at various positions of biphenyl molecule were determined from the Kováts indexes of the corresponding methyl- and ethylbiphenyls. With the use of these increments then the theoretical Kováts indexes of methylethyl- and trimethylbiphenyls were calculated. The measurements results of the elution indexes with various stationary phases were processed statistically. According to ref.¹³ the connectivity indexes of trimethyl- and methylethylbiphenyls were calculated and their correlation with the elution indexes was studied.

RESULTS AND DISCUSSION

The Kováts indexes calculated either from experimental elution data from three capillary columns or from the increments are given in Tables II (trimethyl- and methylethylbiphenyls) and III (methyl-, ethyl- and dimethylbiphenyls). Reproducibility of the Kováts indexes determination varied within two units for all the three stationary phases. From the tables it follows that increasing selectivity of the stationary phase results in increasing number of the alkylbiphenyls eluted before the parent biphenyl.

TABLE I

The Capillary Columns Used for Analyses of Trimethyl- and Methylethylbiphenyls

Number of column	<i>L</i> m	(i.d.) mm	Preparation of the column surface before wetting	Stationary phase	Number of theor. plates ^a
1	50	0.25	etched with methyl 1,1,2-trifluorochloroethyl ether	Apiezon L (C. Erba)	65 000
2	25	0.25	graphitized carbon black (according to ref. ¹²)	<i>m</i> -bis(phenoxy-phenoxybenzene)	27 000
3	41	0.25	etched with methyl 1,1,2-trifluorochloroethyl ether	Reoplex 400 (Appl. Science)	53 000

^a The number of theoretical plates was determined for $k = 2.5$ for all the three columns.

TABLE II

The Experimentally Found and the Theoretically Calculated Kováts Elution Indexes of Trimethyl- and Methylethylbiphenyls

Isomer	I_{APL}^a		I_{BPB}^b		I_{REO}^c		Method of calculation
	exp.	theor.	exp.	theor.	exp.	theor.	
Trimethylbiphenyls							
2,6,2'-	1 486	1 466	1 673	1 661	1 933	1 899	$I_{2,6}^d + \Delta I_2^e -$
2,5,2'-	1 538	1 534	1 736	1 747	1 996	2 008	$I_{2,5} + \Delta I_2 -$
2,6,3'-	1 543	1 559	1 746	1 764	2 018	2 068	$I_{2,6} - + \Delta I_3 -$
2,4,2'-	1 552	1 536	1 752	1 752	2 033	2 019	$I_{2,4} - + \Delta I_2 -$
2,3,2'-	1 566	1 558	1 773	1 780	2 058	2 049	$I_{2,3} - + \Delta I_2 -$
2,6,4'-	1 568	1 571	1 776	1 778	2 058	2 079	$I_{2,6} - + \Delta I_4 -$
3,5,2'-	1 612	1 632	1 833	1 862	2 131	2 151	$I_{3,5} - + \Delta I_2 -$
2,5,3'-	1 626	1 632	1 839	1 850	2 150	2 177	$I_{2,5} - + \Delta I_3 -$
2,4,3'-	1 632	1 639	1 851	1 855	2 160	2 188	$I_{2,3} - + \Delta I_3 -$
2,5,4'-	1 645	1 644	1 862	1 864	2 174	2 188	$I_{2,5} - + \Delta I_4 -$
2,4,4'-	1 651	1 651	1 870	1 869	2 183	2 199	$I_{2,4} - + \Delta I_4 -$
2,3,3'-	1 652	1 661	1 875	1 883	2 193	2 218	$I_{2,3} - + \Delta I_3 -$
3,4,2'-	1 669	1 674	1 885	1 882	2 208	2 224	$I_{3,4} - + \Delta I_2 -$
2,3,4'-	1 671	1 673	1 896	1 897	2 216	2 229	$I_{2,3} - + \Delta I_4$
3,5,3'-	1 739	1 739	1 971	1 976	2 319	2 320	$I_{\text{bif}}^f + 3 \cdot \Delta I_3 -$
3,5,4'-	1 748	1 751	1 984	1 988	2 329	2 331	$I_{\text{bif}}^f + 2 \cdot \Delta I_3 - + \Delta I_4 -$
3,4,3'-	1 776	1 777	2 020	2 020	2 380	2 393	$I_{3,4} - + \Delta I_3 -$
3,4,4'-	1 787	1 789	2 031	2 032	2 392	2 404	$I_{3,4} - + \Delta I_4 -$
Methylethylbiphenyls							
2,2'-	1 509	1 488	1 722	1 698	1 981	1 930	$I_{\text{bif}} + \Delta I_{2-\text{Mc}} + \Delta I_{2-\text{Et}}^g$
3,2'-	1 568	1 591	1 787	1 803	2 073	2 081	$I_{\text{bif}} + \Delta I_{3-\text{Mc}} + \Delta I_{2-\text{Et}}$
4,2'-	1 593	1 603	1 813	1 815	2 101	2 120	$I_{\text{bif}} + \Delta I_{4-\text{Mc}} + \Delta I_{2-\text{Et}}$
2,3'-	1 599	1 614	1 828	1 842	2 118	2 143	$I_{\text{bif}} + \Delta I_{2-\text{Mc}} + \Delta I_{3-\text{Et}}$
2,4'-	1 623	1 638	1 852	1 870	2 147	2 169	$I_{\text{bif}} + \Delta I_{2-\text{Mc}} + \Delta I_{4-\text{Et}}$
3,3'-	1 716	1 717	1 948	1 947	2 311	2 312	$I_{\text{bif}} + \Delta I_{3-\text{Mc}} + \Delta I_{3-\text{Et}}$
4,3'-	1 729	1 729	1 964	1 959	2 301	2 323	$I_{\text{bif}} + \Delta I_{4-\text{Mc}} + \Delta I_{3-\text{Et}}$
3,4'-	1 740	1 741	1 975	1 975	2 318	2 339	$I_{\text{bif}} + \Delta I_{3-\text{Mc}} + \Delta I_{4-\text{Et}}$
4,4'-	1 752	1 753	1 986	1 987	2 331	2 350	$I_{\text{bif}} + \Delta I_{4-\text{Mc}} + \Delta I_{4-\text{Et}}$

The used symbols: The Kováts elution index with the column wetted with ^a Apiezon L, ^b *m*-bis-(*m*-phenoxyphenoxy)benzene, ^c Reoplex 400. The Kováts elution index ^d ($I_{x,y}$) of *x,y*-dimethylbiphenyl, ^e increment of methyl group at *z*-position ($z = 2-4$), ^f the Kováts elution index of biphenyl. ^g $I_{x-\text{Et}}$ and $I_{x-\text{Mc}}$ — the increments of methyl and ethyl groups, respectively, at *x*-position ($x = 3, 4$).

This fact has already been mentioned in ref.⁸. In the case of 2-methylbiphenyl and 2,6-dimethylbiphenyl the elution order of peaks of these compounds from the column containing *m*-bis(*m*-phenoxyphenoxy)benzene is changed as compared with the data given in ref.⁸. The change can be ascribed either to the fact that we were using glass capillary columns instead of columns of stainless steel⁸ or rather to the fact that we modified the inner surface of the capillary column with a layer of graphitized carbon black before wetting. Consequently the elution would be subject (at least to a limited extent) to effects typical of gas-liquid-solid chromatography. It is,

TABLE III
The Kováts Elution Indexes of Methyl-, Ethyl- and Dimethylbiphenyls

Hydrocarbon	I_{APL}^a	I_{BPB}	I_{REO}
Biphenyl	1 445	1 676	2 045
Methylbiphenyls			
2-	1 440	1 671	1 974
3-	1 543	1 790	2 144
4-	1 555	1 802	2 154
Ethylbiphenyls			
2-	1 493	1 703	2 012
3-	1 619	1 847	2 215
4-	1 643	1 875	2 240
Dimethylbiphenyls			
2,2'	1 447	1 654	1 953
2,6-	1 461	1 666	1 970
2,3'-	1 524	1 747	2 062
2,5-	1 534	1 752	2 079
2,4-	1 541	1 757	2 090
2,4'-	1 546	1 762	2 087
2,3-	1 563	1 785	2 120
3,5-	1 637	1 867	2 222
3,4'-	1 654	1 880	2 245
4,4'-	1 664	1 890	2 254
3,4-	1 679	1 916	2 295

^a For the symbols see Table II.

however, impossible to exclude combined operation of the both mentioned factors. From Table II it follows (by comparison of the Kováts indexes of 2-methyl-4'-ethylbiphenyl and 4-methyl-2'-ethylbiphenyl, 3-methyl-4'-ethylbiphenyl and 4-methyl-3'-ethylbiphenyl in a column wetted with Apiezon L) that out of the mentioned pairs of compounds those with 4-ethyl group will be higher boiling due to lengthening of the molecule. The same is true of the pair 2-methyl-3'-ethylbiphenyl and 3-methyl-2'-ethylbiphenyl, too, the compound with ethyl group at a position more distant from 1-position having higher elution index. Table IV gives the parameters of mutual

TABLE IV

Parameters of Linear Dependences $I_{ApL} = k \cdot I_{stat.phase(2)} + q$ and the Respective Correlation Coefficients r

Hydrocarbons	Stationary phase (2)					
	<i>m</i> -bis(<i>m</i> -phenoxyphenoxy)benzene			Reoplex 400		
	<i>k</i>	<i>q</i>	<i>r</i>	<i>k</i>	<i>q</i>	<i>r</i>
Methylbiphenyls	0.8729	-18.65	0.9999	0.6243	207.5	0.9990
Ethylbiphenyls	0.8730	-18.94	0.9999	0.6436	197.7	0.9988
Dimethylbiphenyls	0.9003	-42.10	0.9990	0.6969	87.2	0.9989
Methylethylbiphenyls	0.9210	-79.10	0.9995	0.6881	144.8	0.9989
Trimethylbiphenyls	0.851	58.50	0.9997	0.6494	231.5	0.9994

TABLE V

Increments of the Kováts Indexes for the Capillary Columns Used for Analyses

Alkyl group	Stationary phase		
	Apiezon L	<i>m</i> -bis(<i>m</i> -phenoxyphenoxy)benzene	Reoplex 400
2-Methyl-	-5	-5	-71.5
3-Methyl-	98	100	97.5
4-Methyl-	110	112	109
2-Ethyl-	48	27	-33.7
3-Ethyl-	174	171	169.1
4-Ethyl-	198	199	196

linear dependences between the elution indexes from the columns wetted with phases of different polarities obtained by the least squares method along with the correlation coefficients. Certain differences in slopes of these dependences are obviously due to transition from monosubstituted to polysubstituted alkyl homologues. However, these differences are not distinct enough to enable precise classification of the alkylation degree in the biphenyl molecule.

From Tables II and III it follows that the elution order of x, y, z' -trimethylbiphenyls (x, y, z' denoting the position of alkyl substituent) is identical with that of x, y -dimethylbiphenyls. Out of the given trimethylbiphenyls, according to the expectations, those substituted at $x, y, 2'$ -positions are eluted first, being followed by $x, y, 3'$ - and then $x, y, 4'$ -substituted ones. This order applies invariably to all the three columns used.

The increments of the Kováts indexes due to the presence of methyl or ethyl group at various positions of biphenyl molecule for the used stationary phases are given in Table V, and the therefrom calculated Kováts indexes of methylethylbiphenyls

TABLE VI
Connectivity Indexes of Trimethylbiphenyls (I) and Methylethylbiphenyls (II)

Isomers I	Indexes	Isomers II	Indexes
2,3,2'-	3·2382	2,2'-	5·1767
2,3,3'-	3·5655	2,3'-	5·1707
2,3,4'-		3,2'-	
3,4,3'-		2,4'-	5·4593
3,4,4'-	3·5594	4,2'-	
2,5,3'-		3,3'-	5·2653
2,5,4-			
2,4,2'-	5·5414	3,4'-	
2,4,3'-		4,4'-	5·4534
2,4,4'-	5·8687	4,3'-	
2,6,2'-	2·9880	—	—
2,6,3'-		—	—
2,6,4'-	3·3154		
3,5,2'-	3·2261	—	—
3,5,3'-		—	—
3,5,4'-	3·5534		
3,4,2'-		—	—
2,5,2'-	3·2321		

and trimethylbiphenyls are given in Table II. From the latter it is seen that the indexes of the methylethylbiphenyls with the alkyl groups at 3- and 4-positions of the both aromatic rings can be predicted with sufficient accuracy. In the same way it is possible to determine (with the accuracy of ± 3 units) the indexes of only two trimethylbiphenyls, because in all the other cases at least one methyl group is at 2-position or at *o*-position to another methyl group. Similarly, in the remaining methylethylbiphenyls there is at least one alkyl group at 2-position. These facts are obviously responsible for the deviations between the theoretically calculated and the experimentally found elution indexes of these compounds. The indexes of some further trimethylbiphenyls can be calculated with sufficient accuracy by addition of the methyl group increment to the experimentally found elution index of the corresponding dimethylbiphenyl. For more accurate calculation it is necessary to choose that one of the alternative dimethylbiphenyls which carries the both methyl groups in one aromatic ring. This procedure eliminates at least partially the error due to addition of the 2-methyl group increment or mutual influence of methyl groups (or their increments) present in the same aromatic ring. Nevertheless accuracy of the prediction in most cases goes below 10 units of the elution index. It can be presumed, too, that an even worse agreement between the found and the calculated elution indexes will exist in the case of tetramethylbiphenyls. The given procedure was applied successfully to prediction of the elution indexes of most trimethyl- and methylethylbiphenyls in the columns wetted with Apiezon L and *m*-bis(*m*-phenoxyphenoxy)benzene, whereas with the polar phase Reoplex 400 the obtained agreement was worse than 10 units of elution index. The increments obtained from elution data of methyl- and ethylbiphenyls on a polar stationary phase do not obviously express with sufficient accuracy the overall change of polarity of the molecule due to the presence of several alkyl groups. This statement can be supported by the fact that the theoretically calculated Kováts indexes of trimethylbiphenyls for the stationary phase Reoplex 400 differ from the experimental values by more than 10 units of the elution index in about 80% of cases, whereas for Apiezon L and *m*-bis(*m*-phenoxyphenoxy)benzene the same is true in about 25% of cases only. It is likely that two methyl groups present in mutual *ortho* positions affect the polarity of the trimethylbiphenyl molecule more significantly than the mere increments of methyl groups would suggest, which results in an inaccurate assessment of the Kováts indexes of the mentioned compounds for the column wetted with Reoplex 400. The theoretically calculated elution indexes only agreed with the experimental ones in two cases (3,5,3'- and 3,5,4'-trimethylbiphenyl).

From Table VI it is seen that the connectivity indexes cannot be correlated with the elution behaviour of trimethylbiphenyls, because in a number of cases (*x, y, 3'*- and *x, y, 4'*-trimethylbiphenyls) one connectivity index was obtained for two various isomers. The mentioned quantity does not fully express, in this case, the effect of structure of the studied compounds on their elution in the capillary GLC.

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