GEL CHROMATOGRAPHY OF ADAMANTANE HYDROCARBONS

S.Hála, K.Pecka and B.Kremanová

*Department of Petroleum Technology and Petrochemistry, and
Laboratory of Synthetic Fuels, Institute of Chemical Technology, 166 28 Prague 6*

Elution volumes of thirty polycycloalkanes with adamantane and other structures were determined for gel chromatography on styrene–divinylbenzene gel in tetrahydrofuran. Elution volumes of methyl ethyladamantanes substituted on bridge heads can be determined on the basis of alkyl increments. In the series of polycycloalkanes of various structures a linear relationship between the distribution constants and effective molecular diameters has been established. A linear correlation has also been found between the elution volumes of isomeric tricycloalkanes and their relative enthalpies calculated from conformational analysis.

Polycycloalkanes which constitute a considerable proportion of heavy mineral oil fractions are still little investigated because in consequence of the high number of existing isomers they represent the most complex structural class of hydrocarbons occurring in petroleum. For the separation of complex hydrocarbon fractions of this type methods are advantageous that permit the separation of the mixtures on the basis of the size or the shape of the molecule. In our preceding papers[1-3] in which we studied the methods of analysis of polycycloalkanes with adamantane structure we found two methods, *viz.* extractive crystallization with thiocarbamide[4] and thermodiffusion[5], as suitable for the isolation of adamantane hydrocarbons from petroleum. In this paper we tested on model substances the method of gel chromatography for the separation of adamantane hydrocarbons.

Gel chromatography was used originally predominantly for the separation of polymers and other macromolecules. Today, when gels with low exclusion limit are available gel chromatography may also be employed for the separation of smaller molecules. In the separation of hydrocarbon mixtures the elution of components is directed by the effective molecular volume exclusively[6]. The following factors are mentioned in literature as having a bearing on the effective volume of molecules and which are in correlation with the elution volumes of hydrocarbons: the length of the hydrocarbon chain[7,8], molar volume[9,10], molecular mass[11] and various dimensions of molecular models[12]. Schulz[13] found in isoalkanes a relationship between the molar volume and the average number of synclinal (gauche) butane interactions in the molecule, which enables the computation of the elution data from the structure and the conformation. The majority of the relationships mentioned was inferred from the elution volumes of alkanes and aromatic hydrocarbons. No detailed data are available on gel chromatography of saturated polycyclic hydrocarbons.

EXPERIMENTAL

Apparatus and Measurement Procedure

For the measurement a liquid chromatograph of common construction was used: model LC-I (Development Centre of Natural Sciences Faculty, Charles University, Prague), provided with a 6 m long column of 8 mm internal diameter, packed with styrene–divinylbenzene gel S-Gel-832 (Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague) of 32—48 µm particle size, exclusion limit 1 000 units of molecular mass. As mobile phase dried and recti-fied tetrahydrofuran was employed which was pumped under 10—11 atm pressure and room temperature through the column at a volume rate of 16—17 ml/h. A differential refractometer detector with cell temperature of $30 \pm 0.1°C$ was used, which was connected with a line recorder and a photoelectric device for the registration of the mobile phase volume (1 count = 2·60 ml). The hydrocarbon samples were injected into the column with a syringe (about 0·5 ml), in the form of a 0·75% solution in tetrahydrofuran. Elution volumes (V_e) of hydrocarbons were read from the maxima of the recorded peaks. The round values of the elution volumes given in Table I were obtained from two to four independent measurements which did not differ by more than 1% relative. The efficiency of the gel column was calculated in the conventional manner and it was 25 600 TP for n-pentane, corresponding to HETP = 0·23 mm.

For the calculation of the distribution constant K_d of the measured hydrocarbons from the equation

$$V_e = V_0 + K_d V_i , \qquad (1)$$

the outer volume of the gel column was measured using polystyrene standard, and the value $V_0 = 100$ ml was obtained. For the inner volume of the gel on the column the value $V_i = 120$ ml was used which was calculated from the elution volume of cyclopentane (220 ml) under the sup-position that for cyclopentane (the molecule of which differs from that of tetrahydrofuran only negligibly) the distribution constant K_d may be assumed to be equal to one. During the measure-ment of the elution volumes of hydrocarbons composed of several isomers which did separate on the gel column, the sequence of elution of single isomers was controlled by the effluent analysis with gas chromatography on capillary columns.

The effective diameters of the molecules of the measured hydrocarbons were calculated as averages of six dimensions of molecular models constructed from Stuart and Briegleb space-filling atomic models (E. Leybold's Nachfolger, Köln-Bayental) on the 1 cm = 0·67 Å scale. The proce-dure of the measurements consisted in locating the centre of the molecular model at the ideal cross-section of rectangular coordinates and measuring the maximum dimension of the molecular projection in the direction of the x axis, and the second dimension of the same projection, which is perpendicular to the maximum dimension. In the same manner the dimensions of the projections were then measured in the direction of the axes y and z. Maximum dimensions of the projections correspond to the diameter of a cylinder through which the molecular model can just pass in the given orientation. The measurements are hampered by an error of about 10% relative.

Hydrocarbons Tested

The procedures for the preparation of the adamantane (*1*), diamantane (*2*), homoadamantane (*3*), alkyladamantanes *5*, *6*, *8* and *10—18* are given in the preceding communication[14]. 1,2-Tetra-methyleneadamantane (*4*) was isolated from the isomerization product of the photodimer of nor-bornene to diamantane[15]. For the preparation of 1-phenyladamantane (*7*) the alkylation of ben-zene with 1-bromoadamantane, described earlier[4], was employed. 1,1′-Diadamantyl (*9*) was

prepared[4] on reaction of an ethereal solution of 1-bromoadamantane with sodium powder, and the diadamantyl derivative *19* was prepared analogously from 1-bromo-3-ethyl-5-methyl-adamantane. Among other cycloalkanes tested cyclopentane and decalin were current commercial chemicals. From the reaction products of cyclopentadiene with ethylene[16] diendomethylenedecalin (*21*) and norbornene were prepared. The latter was dimerized on irradiation with ultraviolet light (253·7 nm) from a NFUV-300 lamp (Nester and Faust, U.S.A.) to the pentacyclic hydrocarbon *23*. Both isomers of trimethylenenorbornane (*20*) were prepared by hydrogenation of dicyclopentadiene (L. Light and Co., Ltd.) on Raney-nickel under pressure, using a rotatory steel autoclave; mild isomerization of the product brought the content of the exo-isomer to about 50%. Pressure hydrogenation in the same autoclave was also used for the preparation of cyclododecane from cyclododecatriene (Chemische Werke, Hüls AG.) and perhydroacenaphthene, perhydrophenanthrene and perhydroanthracene from the corresponding aromatics. n-Alkanes which were used for the calibration of the gel column were synthetic standards for gas chromatography. All hydrocarbons measured were analysed by gas chromatography and mass spectrometry.

RESULTS AND DISCUSSION

Unsubstituted cycloalkanes of the same carbon number. From the elution volumes of the hydrocarbons tested (Table I) it follows that the unsubstituted cycloalkanes with the same number of carbon atoms are eluted from the gel column in the order of increasing number of cycles in the molecules. For example, the sequence of C_{10}-hydrocarbons is n-decane, decalin, trimethylenenorbornane (*20*), adamantane; similarly C_{12}-hydrocarbons show the order n-dodecane, cyclododecane, perhydroacenaphthene, diendomethylenedecalin, and C_{14}-hydrocarbons the following order, perhydroanthracene, perhydrophenanthrene, 1,2-tetramethylene-adamantane (*4*), pentacyclotetradecane (*23*), diamantane (*2*). All three hydrocarbons with adamantane structure, mentioned in these sequences — tricyclic adamantane (*1*), tetracyclic derivative *4* and pentacyclic diamantane (*2*) — are eluted at positions corresponding to their number of rings. In the mentioned sequences two pairs of structural isomers are also present: trimethylenenorbornane (*20*) and adamantane, which have the same composition $C_{10}H_{16}$, and a second pair, pentacyclotetradecane (*23*) and diamantane of the composition $C_{14}H_{20}$; in both cases the isomers with the adamantane structure are more retained on the gel column, evidently in consequence of a more compact structure which is reflected in a smaller molecular volume.

Homologous alkyladamantanes. The elution volumes of alkylated adamantanes are the smaller the more substituents carries the adamantane nucleus. The number of substituents has a much higher effect on the elution volume than the size of the substituent; two methyl groups decrease the elution volume more than one ethyl group or a similar group, as may be seen from the decrease in the elution volumes in the sequence 1-methyladamantane (202 ml), 1-ethyladamantane (201 ml), 1-isopropyladamantane (197 ml), in comparison with the sequence 1-methyladamantane (202 ml), 1,3-dimethyladamantane (194 ml), 1,3,5-trimethyladamantane (186 ml). In adamantanes with cyclic substituents, as for example 1-phenyladamantane or

TABLE I

Elution Volumes (V_e) and Distribution Constants (K_d) of Adamantanes and Other Hydrocarbons

No	Hydrocarbon	Formula	V_e, ml	K_d
	Adamantanes			
1	adamantane	$C_{10}H_{16}$	214	0·95
2	diamantane	$C_{14}H_{20}$	214	0·95
3	homoadamantane	$C_{11}H_{18}$	212	0·93
4	1,2-tetramethyleneadamantane	$C_{14}H_{22}$	205	0·88
5	2-ethyladamantane	$C_{12}H_{20}$	203	0·86
6	1-methyladamantane	$C_{11}H_{18}$	202	0·85
7	1-phenyladamantane	$C_{16}H_{20}$	202	0·85
8	1-ethyladamantane	$C_{12}H_{20}$	201	0·84
9	1,1′-diadamantyl	$C_{20}H_{30}$	200	0·83
10	1-isopropyladamantane	$C_{13}H_{22}$	197	0·81
11	1,3-dimethyladamantane	$C_{12}H_{20}$	194	0·78
12	1-(2′-butyl)adamantane	$C_{14}H_{24}$	193	0·78
13	1-ethyl-3-methyladamantane	$C_{13}H_{22}$	192	0·77
14	1,3-diethyladamantane	$C_{14}H_{24}$	189	0·74
15	1,3,5-trimethyladamantane	$C_{13}H_{22}$	186	0·72
16	1-ethyl-3,5-dimethyladamantane	$C_{14}H_{24}$	184	0·70
17	1,3,5,7-tetramethyladamantane	$C_{14}H_{24}$	178	0·65
18	1-ethyl-3,5,7-trimethyladamantane	$C_{15}H_{26}$	176	0·63
19	3,3-diethyl-5,5′-dimethyl-1,1′-diadamantyl	$C_{26}H_{42}$	166	0·55
	Other polycycloalkanes			
20a	endo-trimethylenenorbornane	$C_{10}H_{16}$	213	0·94
20b	exo-trimethylenenorbornane	$C_{10}H_{16}$	209	0·91
21	diendomethylenedecalin	$C_{12}H_{18}$	212	0·93
22a	*cis* decalin	$C_{10}H_{18}$	208	0·90
22b	*trans*-decalin	$C_{10}H_{18}$	203	0·86
23	dimer of norbornene	$C_{14}H_{20}$	206	0·86
24	perhydroacenaphthene[a]	$C_{12}H_{20}$	201	0·84
25	perhydrofluorene[a]	$C_{13}H_{22}$	197	0·81
26	cyclododecane	$C_{12}H_{24}$	196	0·80
27	perhydrophenanthrene[a]	$C_{14}H_{24}$	194	0·78
28	perhydroanthracene[a]	$C_{14}H_{24}$	192	0·77
	Calibration hydrocarbons			
	cyclopentane		220	1·000[b]
	n-pentane		204	0·87
	n-heptane		191	0·76
	n-nonane		180	0·67
	n-undecane		172	0·60
	n-dodecane		169	0·58

[a] The most stable isomer; [b] according to definition.

1,1'-diadamantyl, these bulky substituents cause practically the same decrease in the elution volume as methyl or ethyl. The increase of the ring in the adamantane structure, or the condensation of another ring to it (as in hydrocarbon 4) has a still weaker effect than the methyl group. The dependence of the elution volume on the structure in the series of alkyladamantanes with methyl and ethyl substituents on tertiary carbon atoms (in the positions 1, 3, 5, 7) is simple because in view of the small range of molecular masses linear correlations are satisfactory. From the dependence of V_e on the number of carbon atoms, shown in Fig. 1, it is evident that by connecting the points for alkyladamantanes 6, 8, 11 and 13 − 18 a segment of a network graph is formed in which it is shown that each further methyl substituent on the nucleus causes a constant decrease of the elution volume by 8 ml and that each ethyl substituent decreases it by 10 ml. The dependence of the elution volumel in these methyl- and ethyl-substituted adamantanes may be expressed for a given get system by the simple equation

$$V_e = 210 - 8M - 10E,\qquad(2)$$

where M is the number of methyls and E the number of ethyls on the bridge heads of the adamantane nucleus. In an earlier paper[14] we found that in gas chromato-
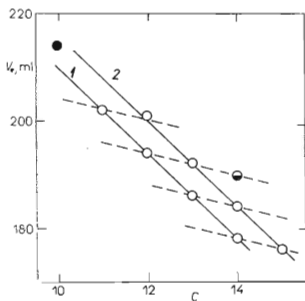

FIG. 1

Dependence of Elution Volumes of Some Alkyladamantanes on the Carbon Number (C)

1 Methyladamantanes (6, 11, 15, 17), 2 ethylmethyladamantanes (8, 13, 16, 18), ● adamantane, ◒ 1,3-diethyladamantane.
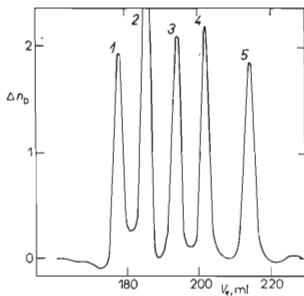
FIG. 2

Separation of a Mixture of Methylated Adamantanes on a Gel Column

1 Tetramethyladamantane (17), 2 trimethyladamantane (15), 3 dimethyladamantane (11), 4 methyladamantane (6), 5 adamantane.

graphy of alkyladamantanes the differences of the elution indexes on a polar or non-polar phase may be calculated on the basis of alkyl increments using a similar relationship. We expect that the equation (2) will be useful for the prediction of the elution volumes of the remaining five methyl ethyladamantanes. The differences in the elution volumes caused by homologous increments suffice for a very good separation of single members of the homologous series studied. As may be seen from Fig. 2 representing the record by a differential refractometer of a separated mixture of adamantane and four methylated adamantanes 6, 11, 15 and 17, gel chromatography enables the separation of this mixture with an efficiency which is comparable with the efficiency of a gas chromatography. The peak resolution (r) of a gel column, calculated according to the relationship employed in gas chromatography[17], is listed for neighbouring pairs of components in Fig. 2 in the range $r = 1\cdot3 - 2\cdot1$ (at a 100% separation $r = 1\cdot5$).

Dependence of K_d on the effective molecule diameter. For the explanation of the separation mechanism of gel chromatography Porath[18] proposed a model based on the idea that the cavities inside the gel have a conical shape, so that only a part of the inner volume is accessible for the solute molecules of spherical shape, proportional to the size of the entrance opening and the diameter of the solute molecule. For the distribution constant K_d which is defined as the ratio of the utilisable internal volume of the gel and the total internal volume of the swelled gel, and for this model the following relationship is obtained

$$K_d = k(1 - R/A)^c , \qquad (3)$$

where R is the diameter of the molecule, A is the diameter of the entrance opening, k is proportionality factor and the exponent c has the value $c = 3$ for the conical shape of the cavities. For other geometrical shapes of the inner space of the gel the exponent has the following values: $c = 3$ for spherical hollows, $c = 2$ for cylindrical cavities, and $c = 1$ for slits.

The hydrocarbons with adamantane structure when compared with other low-molecular organic compounds are very suitable models for the checking of the exclusion theory of gel chromatographic separation. In addition to the fact that these compounds are unpolar they have a compact, rigid structure which is in the case of some hydrocarbons so symmetrical (adamantane, tetramethyladamantane 17) that they very nearly approach to the ideal spherical form. Therefore, we investigated to what extent the elution data of adamantanes and other polycycloalkanes agree with the relationship (3). We computed the values K_d from equation (1) on the basis of an approximate value for V_i, determined with cyclopentane which is structurally most similar to tetrahydrofuran and for which it may be supposed that it has at its disposal the same internal volume of the gel as the solvent.

During the study of the correlations between the elution volume and the size of the molecule the general question arises which dimension expresses best the size of an asymmetrical molecule. From the comparison of the molecular models of adamantane, 1-methyladamantane, 1-phenyladamantane and 1,1'-diadamantyl it is evident that neither the minimal nor the maximal dimension of the molecule in itself is in correlation with the elution volume. Adamantane has the same minimum dimension of the molecule as the other three hydrocarbons mentioned, but in spite of this it has a higher elution volume. On the other hand, for example 1-methyladamantane and 1,1'-diadamantyl have approximately the same elution volumes in spite of the fact that the maximum dimension of diadamantyl

TABLE II

Distribution Constants (K_d) of Polycycloalkanes Calculated from Effective Diameters of the Molecules (R) according to Equation (4)

Hydrocarbon[a]	R Å	K_d		Difference %
		measured	calculated	
1	7·0	0·95	0·91	4·2
2	7·5	0·95	0·85	10·5
3	7·3	0·93	0·87	6·5
4	7·8	0·88	0·81	8·0
5	7·5	0·86	0·85	1·2
6	7·4	0·85	0·86	−1·2
7	8·2	0·85	0·77	9·4
8	7·6	0·84	0·84	0·0
9	8·3	0·83	0·75	9·6
10	7·5	0·81	0·85	−4·9
11	7·9	0·78	0·80	−2·6
12	7·7	0·78	0·83	−6·4
13	8·0	0·77	0·79	−2·6
14	8·3	0·74	0·75	−1·4
15	8·4	0·72	0·74	−2·8
16	8·5	0·70	0·73	−4·3
17	8·9	0·65	0·68	−4·6
18	9·0	0·63.	0·67	−6·3
19	10·2	0·55	0·53	3·6
22a	7·0	0·90	0·91	−1·1
22b	7·1	0·86	0·90	−4·7
26	7·5	0·80	0·85	−6·3
27	7·8	0·78	0·81	−3·8
28	7·8	0·77	0·81	−5·2

[a] Numbering as in Table I.

is almost double that of the methyl derivative. Thompson, Sweeney and Ford[12] achieved in gel chromatography of model aromatic hydrocarbons the better agreement between the calculated and the measured elution volumes the more molecular dimensions they used for their calculations. Therefore, we characterized the size of the molecule by an average value of six dimensions measured in three perpendicular planes passing through the gravity center of the molecule. This value, which in symmetrical molecules of spherical shape corresponds to the diameter of the sphere described, expressed in irregular molecules approximately the effective diameter of the molecule, *i.e.* the dimension which determines the magnitude of the space at the gel surface, from which the molecule is excluded in consequence of a random rotation around the gravity centre. The effective diameters of the molecules (R) calculated for all ninteen measured adamantanes and those of other cycloalkanes composed of six-membered rings only, are given in Table II together with the values for K_d. During the checking of equation (3) it was found that the obtained values are most suitable in the simplest form for $c = 1$, so that the dependence of the distribution constant on the effective diameter of the molecules may be expressed by the relationship

$$K_d = a - bR. \qquad (4)$$

The correlation coefficient of this relationship is $r_k = -0.89$ $(r_k$ has the value 0 for a complete independence and for an indirect functional dependence the value $-1)$. The constants of Eq. (4) computed by linear regression are $a = 1.75$ and $b = 0.12$. The distribution constants of hydrocarbons calculated according to equation (4) are compared with experimental values in Table II. The average differences of both values are 4.6% relative. Standard deviation $s = 0.047$. In spite of the complex method of the measurement of the molecular models that we used being only very
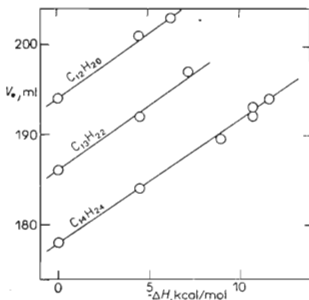

Fig. 3

Correlation of the Elution Volume of Isomeric Tricycloalkanes with Enthalpy

$C_{12}H_{20}$-Hydrocarbons *11, 8, 5*; $C_{13}H_{22}$-hydrocarbons *15, 13, 10*; $C_{14}H_{24}$-hydrocarbons *17, 16, 14, 12, 28, 27.*

approximate, the agreement between the calculated and the measured values is so good that equation (4) may be used for the calculation of practically utilisable data for cycloalkanes $C_{10} - C_{26}$ of different structures, of adamantane and perhydroaromatic type, with various numbers of cycles in the molecules, on the basis of the effective diameter of the molecule. Larger deviations of the calculated values from those measured were found only for hydrocarbons 2, 7 and 9, the molecules of which are most remote from the ideal spherical shape. From equation (4) the effective diameter of flexible molecules on the gel column may also be calculated on the basis of experimental values for K_d. For the measured n-alkanes the following effective diameters of the molecules in Å were obtained: n-pentane 7·3, n-heptane 8·3, n-nonane 9·0, n-undecane 9·6, and n-dodecane 9·8. These values are only 20 − 30% higher than the diameters of tightly coiled n-alkane molecules measured on models by the described procedure.

Correlation of elution volumes of isomeric polycycloalkanes with enthalpy. During a study of gel chromatography of isoalkanes Schulz[13] observed a quantitative relationship between the elution volume and the contribution to the molecular volume caused by each synclinal conformation in the molecule. The demonstrated correlation between the molecular conformation which contributes to the total enthalpy of the substances and the molecular volume which affects the elution in gel chromatography is very important from the practical point of view and it conveys a new view of the separation mechanism. From Auwers rule and conformational rule[19] it follows that in cyclic stereoisomers too the relationship between the molecular volume and the enthalpy is distinctly manifested in various properties. The relationship is indirect because the isomers with a larger molecular volume have smaller non-bonding intra-

TABLE III
Relative Enthalpy and Elution Volumes of Isomeric Tricycloalkanes $C_{14}H_{24}$

Hydrocarbon	Number of			$-\Delta H$ kcal/ /mol	V_e ml
	synclinal interactions	tertiary carbons	quaternary carbons		
1,3,5,7-Tetramethyladamantane	0	0	4	0·0	178
1-Ethyl-3,5-dimethyladamantane	2	1	3	4·5	184
1,3-Diethyladamantane	4	2	2	9·0	189
1-(2'-Butyl)adamantane	5	4	1	10·8	193
Perhydroanthracene (*trans-syn-trans*)	0	4	0	10·8	192
Perhydrophenanthrene (*trans-anti-trans*)	1	4	0	11·7	194

molecular interactions, which is reflected in a lower enthalpy. In view of the demonstrated effect of the molecular volume of hydrocarbons on their elution in gel chromatography we considered it useful to determine the relations between the elution volumes of the polycycloalkanes tested by us and their enthalpies. A few isomers were present among the hydrocarbons tested which are composed of six-membered rings in chair conformation only, for which the differences in enthalpy could be calculated on the basis of a conformational analysis[20,21]. During the calculation of enthalpic differences we used the value 900 cal/mol for the energy contribution of each sinclinal butane conformation and exothermic change in enthalpy, 1800 cal/mol for the formation of a tertiary carbon in the structure, and 2700 cal/mol for the conversion of the tertiary carbon to a quaternary one. The data used for the calculation of the relative enthalpies of six tricyclic isomers of the composition $C_{14}H_{24}$ are given in Table III. Using an analogous procedure[22] and the most stable isomer as basis the differences in enthalpies for three alkyl-adamantane isomers of the composition $C_{13}H_{22}$ were calculated: 1,3,5-trimethyladamantane ($\Delta H = 0$), 1-ethyl-3-methyladamantane (4·5 kcal/mol), and 1-isopropyladamantane (7·2 kcal/mol), and for three adamantane isomers $C_{12}H_{20}$: 1,3-dimethyladamantane ($\Delta H = 0$), 1-ethyladamantane (4·5 kcal/mol) and 2-ethyladamantane (6·3 kcal/mol). As shown in Fig. 3 in all three groups of the cyclic isomers a close linear dependence between the elution volume and the enthalpy was found. These correlations may be useful for the predictions of the separation effect of gel chromatography for fractions containing isomeric polycycloalkanes, and in several cases they also may be used as a complementary method for structural analysis of individual polycycloalkanes.

REFERENCES

1. Hála S., Kuraš M., Landa S.: Neftechim. *6*, 3 (1966).
2. Hála S., Landa S.: Erdöl Kohle *19*, 727 (1966).
3. Hála S., Landa S., Hanuš V.: Angew. Chem. *78*, 1060 (1966).
4. Landa S., Hála S.: This Journal *24*, 93 (1959).
5. Hála S., Kuraš M., Landa S.: Sborník Vysoké školy chemicko-technologické. Praha, *7*, 45 (1964).
6. Freeman D. H.: J. Chromatog. Sci. *11*, 175 (1973).
7. Hendrickson J. G., Moore J. C.: J. Polym. Sci. A—1, *4*, 167 (1966).
8. Hendrickson, J. G.: J. Chromatog. *32*, 543 (1968).
9. Smith W. B., Kollmansberger A.: J. Phys. Chem. *69*, 4157 (1965).
10. Cazes J., Gaskill D. R.: Separ. Sci. *2*, 421 (1967).
11. Oelert H. H., Weber J. H.: Erdöl Kohle *23*, 484 (1970).
12. Thompson R. E., Sweeney E. G., Ford D. C.: J. Polym. Sci. A—1, *8*, 1165 (1970).
13. Schulz W. W.: J. Chromatog. *55*, 73 (1971).
14. Hála S., Eyem J., Burkhard J., Landa S.: J. Chromatog. Sci. *8*, 203 (1970).
15. Bingham R. C., Schleyer P. v. R.: *Recent Developments in the Chemistry of Adamantane and Related Polycyclic Hydrocarbons. Topics in Current Chemistry*, Vol. 18. Springer, Berlin 1971.

16. Plate A. F., Belikova N. A., Kiritschenko S. J.: Neftechim. *1*, 494 (1961).
17. Purnell H.: *Gas Chromatography.* Wiley, New York 1962.
18. Porath J.: Pure Appl. Chem. *6*, 233 (1963).
19. Eliel E. L.: *Stereochemistry of Carbon Compounds.* McGraw-Hill, London 1962.
20. Schneider A., Warren R. W., Janoski E. J.: J. Org. Chem. *31*, 1617 (1966).
21. Petrov A. A.: *Chimija Naftenov.* Nauka, Moscow 1971.
22. Bagrij E. I., Sanin P. I.: Neftechim. *10*, 795 (1970).