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Modelling the Molecular Structures of Petroleum Resins and Asphaltenes and Their Thermodynamic Stability Calculation

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Abstract

Software for constructing the structures of petroleum resins and asphaltenes molecules were developed using Monte Carlo method. With the help of this program, and basing on the parameters of structural group analysis calculated from analytical data concerning elemental composition, molecular mass and PMR spectroscopy, we obtained molecular structures for the resins and asphaltenes of heavy oil from the Zuunbayan (Mongolia) and Usinsk fields. The thermodynamic stability of structures calculated and constructed for the molecules of resin and asphaltene was evaluated using molecular mechanics calculation.

Key words: petroleum resins, asphaltenes, structure modelling

INTRODUCTION

Resins and asphaltenes represent high-molecular heteroatomic compounds contained in oil whose content could be comparable to the total content of alkanes, naphtenes or arenes. Due to their complicated structure, studying them represents an uneasy task. At the same time, visual representation concerning the structure of resins and asphaltenes is very important for using in kinetic models and the models of chemical reactions with their participation, since their role in all the processes from the extraction to processing is extremely great [1].

The spatial structure of the molecules of resins and asphaltenes allows one to estimate their physicochemical properties. Basing on the structures constructed one could perform calculations of such properties as density [2], solubility [3], *etc*. In combination with molecular dynamics, these structures of high-molecular compounds could be used for modelling such processes, as the formation of asphaltene associates and their interaction with solvents [4].

The authors of [1] first for the constructing of resin and asphaltene molecules used the Monte Carlo method that is based on the data obtained from ^{1}H NMR spectroscopy, elemental analysis and molecular mass determination. In the further papers, the mentioned approach has been replenished due to using a great amount of analytical data [5] and the possibility of constructing the structures consisting of linked blocks or monoblock structures with the molecular mass value from 500 to 4000 [6].

The program we have developed for constructing the molecules implies the use of the Monte Carlo method too. However, as the input analytical data, we used the parameters calculated with the application of the structural group analysis [7] those describe the structural fragments of averaged molecules of resins and asphaltenes.

EXPERIMENTAL

We calculated spatial structures for the molecules of resins and asphaltenes obtained from the oil of Zuunbayan (Mongolia) and Usinsk (Russia) fields. Resins and asphaltenes were isolated from oil under investigation using a stan-

dard technique described in [8]. Asphaltenes were isolated by means of precipitation from oil by 40-fold volume of *n*-hexane. The samples were applied onto silica gel ASK, then, using a Soxhlet extractor we successively extracted hydrocarbon components (oils) by *n*-hexane, and resins by benzene + ethanol (1 : 1) mixture.

Structural group analysis (SGA) of the isolated resins and asphaltenes was carried out using the technique developed at the Institute of Petroleum Chemistry, SB RAS (Tomsk) [7, 8]. For SGA we used the data resulted from the analysis of elemental composition, average molecular mass and ^{1}H NMR spectroscopy.

The content of C and H in resins and asphaltenes were determined using the method of combustion, the concentration of nitrogen was determined in a Pokrovsky reactor, and

TABLE 1

Averaged physicochemical and structural parameters of resin and pyrobitumen molecules from the Zuunbayan and Usinsk oil

Parameters	Zuunbayan oil		Usinsk oil	
	Resins	Asphaltenes	Resins	Asphaltenes
Content in oil, mass %	14.7	0.2	18.0	8.1
Molecular mass	1360	2365	830	1550
Elemental composition, mass %:				
C	84.5	87.3	81.3	84.1
H	9.6	10.3	9.3	9.3
N	0.9	1.2	1.6	1.7
S	0.3	0.2	2.9	3.3
O	4.7	1.0	4.9	1.5
Number of atoms in an averaged molecule:				
C	96.7	172.1	56.1	108.5
H	123.3	241.2	76.6	142.9
N	0.8	2.0	0.9	1.9
S	0.1	0.2	0.8	1.6
O	3.7	1.4	2.6	1.5
Number of blocks in a molecule (m_a)	2.2	3.9	1.9	3.5
Ring composition:				
K_t	17.7	24.2	7.7	11.9
K_{ar}	10.8	13.4	5.1	11.9
K_n	6.9	10.8	2.6	0.0
Fraction of five-membered rings (q)	0.17	0.11	0.19	0.21
Distribution of C atoms, %:				
f_{ar}	25.5	33.0	37.4	48.3
f_n	27.5	25.8	18.3	0.0
f_{al}	47.0	41.2	44.3	51.7
Number of different type carbon atoms of **???** in an averaged molecule:				
C_{ar}	24.7	56.7	20.9	52.4
C_n	26.6	44.5	10.3	0.0
C_{al}	45.4	70.9	24.8	56.1
C_α	13.6	20.8	8.0	15.2
C_γ	4.4	11.9	5.4	6.6

Note. C_{ar} – aromatic carbon; C_n – carbon in naphtene rings; C_{al} – carbon in aliphatic chains; C_δ – carbon in α-position with respect to the a ring; C_γ – carbon in terminal methyl groups; K_t – the total number of rings; K_{ar} – the number of aromatic rings; K_n – the number of naphtene rings.

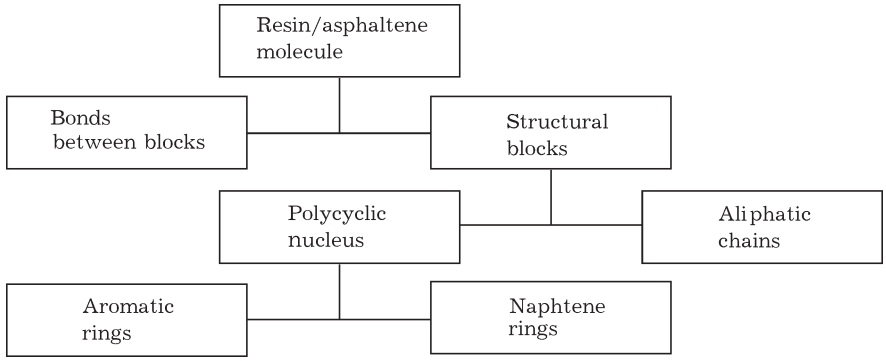

Fig. 1. Scheme of constructing the molecules of resins and asphaltenes specified in the program.

the content of sulphur using the method of double combustion. The molecular mass value was measured by means of cryoscopy in naphthalene using a Krion instrument (IPC, SB RAS, Tomsk). ^{1}H NMR spectra were recorded on a Bruker AVANCE AV-300 FT NMR spectrometer (the solvent was deuterochlorophorm, the internal standard was hexamethyldisiloxane), the concentration of substances being of 1 %.

Table 1 demonstrates SGA data for resins and asphaltenes of oil under study.

The program for the construction of molecules was composed using Compaq Visual Fortran Version 6.6. The calculation of thermodynamic parameters for the molecules constructed was made with the use ChemOffice CS Chem3D 8.0 software. The energy minimization for the molecule constructed as well as the calculation of the total steric energy were carried out using the methods of molecular mechanics (MM2) and molecular dynamics.

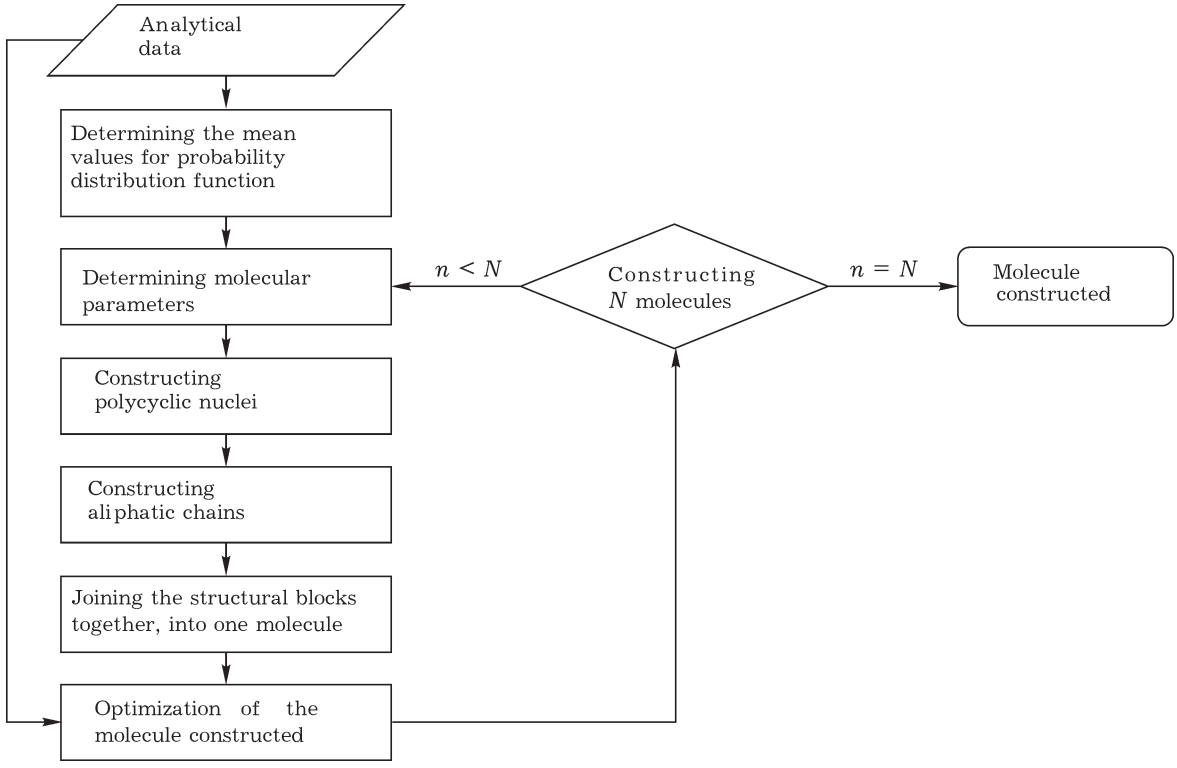

Fig. 2. Algorithm for constructing the molecules of resins and asphaltenes (n is number of construction, N is the total number of construction procedures in the course of the program operation).

SPATIAL CONSTRUCTION OF THE MOLECULES OF RESINS AND ASPHALTENES

The program for the construction of molecules is based on the approach described in [6], with the use of the Monte Carlo method according to the logic diagram for the imaging of resins and asphaltenes (Fig. 1). The molecule of a high-molecular compound consists of the structural blocks linked among themselves with aliphatic chains and heteroatoms. The structural blocks, in turn, consist of a polycyclic nucleus containing aromatic and naphtene rings, and aliphatic chains. The structure of the polycyclic nucleus, aliphatic chains and bonds between the blocks includes sulphur, nitrogen and oxygen heteroatoms.

Figure 2 demonstrates the program operation algorithm. As the input parameters for the program we used analytical data resulted from the elemental analysis, ^{1}H NMR spectroscopy, molecular mass determination, as well as parameters calculated by means of the SGA method.

Each structural parameter of the logic diagram (see Fig. 1) is connected with the probabilistic distribution function that can be preset basing on analytically certain values or γ-distribution (density function). The possibility of using the γ-distribution for the construction of such complex molecules as petroleum resins and asphaltenes was demonstrated by the authors of [1, 9, 10].

In order to determine each parameter, the following procedure was used. Firstly, the program generates a random number from 0 up to 1. Further, from the distribution function we determined the value the parameter under consideration using a random number as the argument of the function. The γ-distribution represents a function certain within the range of values [0, +∞], therefore an approach should be developed, wherein the γ-distribution would be transformed for the parameter determined according to minimal, maximal and average values of the parameter.

The polycyclic nucleus of each structural block is determined by the probabilistic distri-

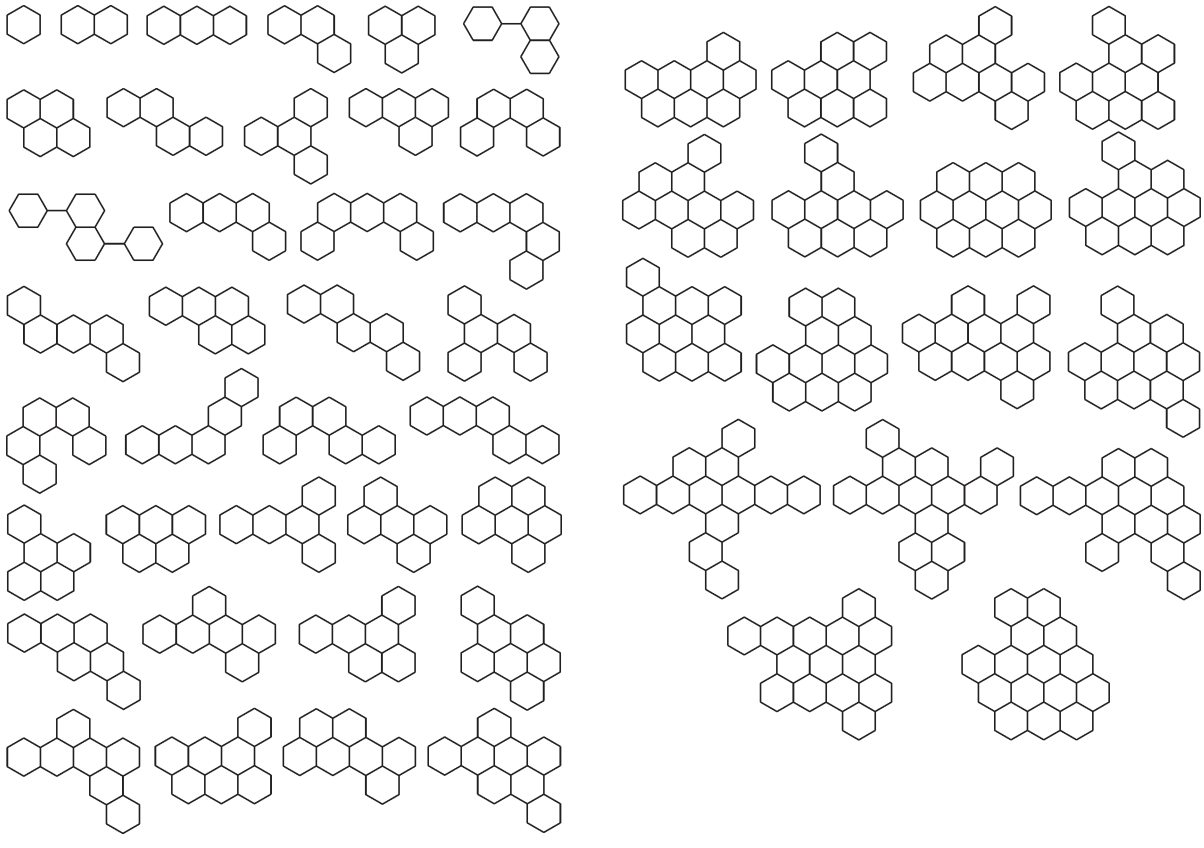

Fig. 3. Polycyclic structures, whose presence in oil it is proved.

TABLE 2

Optimization parameters

Nos.	Parameters
1	Molecular mass
2	C, mass %
3	H, mass %
4	N, mass %
5	S, mass %
6	O, mass %
7	C aromatic, %
8	C naphtene, %
9	C aliphatic, %
10	C-α, %
11	C-γ, %

bution functions from the library (Fig. 3), wherein almost all the possible structures are contained inherent in oil. The mentioned library is made basing on data [5, 11, 12]. The two approaches to the construction of polycyclic nuclei for high molecular mass molecules are known. The first one consists in determining the number of aromatic and naphtene carbon atoms with the subsequent joining together into one structure. The second approach is based on the preliminary determination of probable polycyclic structures, wherefrom the choice is made for the construction of a molecule in the course of the program running.

In our opinion, the second approach is much more rational, since it allows one to preset the certain polycyclic structures, to reduce the calculation tome to a considerable extent, as well as to exclude the possibility of constructing the structures by the program those could not really exist or whose existence is thermodynamically improbable for petroleum resins and asphaltenes.

Owing to the absence of any literature data concerning the distribution of heteroatoms throughout functional groups in the molecules of resins and asphaltenes, we assumed the following ratio values: 50 % benzo-, dibenzothiophene and 50 % sulphide groups for sulphur atoms; 50 % quinoline, benzoquinoline and 50 % weakly basic and neutral groups for nitrogen; 1/3 ether (ester) oxygen, 1/3 carbonyl oxygen atoms and 1/3 phenolic and furan oxygen for oxygen [8].

After determining all the parameters and their joining together into one molecule, we determined the difference F between the parameters of a real sample determined analytically (see Table 1), and the parameters of the model constructed. The procedure of optimization was performed according to the formula

$$F = \sum_{m=1}^{6} \left(\frac{\mu'_m - \mu_m}{\sigma_m}\right)^2 + \frac{1}{11} \sum_{m=7}^{11} \left(\frac{\mu'_m - \mu_m}{\sigma_m}\right)^2$$

Here μ'_m is the parameter of the molecule constructed; μ_m is the parameter determined analytically; σ_m is the property error calculated; m is the number of the parameter. Table 2 demonstrates the list of parameters used.

Due to a repeated construction of molecules during the program operation, finding a molecule with parameters the most close to a real sample and with a minimal deviation (see Fig. 2) is attained In the course of the calculations the parameter $N = 1000$.

Table 3 presents data concerning the five variants of structures constructed for the molecules of resins and asphaltenes from the Zuunbayan and Usinsk oil, as well as data on the values of difference calculated.

Figures 4 and 5 demonstrate the images of petroleum resin and asphaltenes molecules with minimal parameter F values.

It should be noted, that the indeterminacy in the types of heteroatomic groups both in resins and asphaltenes results in an increase in the discrepancy between the parameters calculated according to the program and those determined analytically. In this connection, the deviation for resins and asphaltenes of the Usinsk oil is much greater than that for the Zuunbayan oil. It could be connected with a higher content of heteroatoms herein, whose functional nature is not studied up till now.

Special investigations are necessary in order to increase the reliability of calculation methods for determining the geometrical structure of molecules of heteroatomic groups and their steric effects on the spatial structure of resins and asphaltenes.

TABLE 3

Parameters of molecules constructed for high molecular mass compounds from the Zuunbayan and Usinsk oil

Nos.	Parameters	Resins					Asphaltenes				
		Molecule number					Molecule number				
		1	2	3	4	5	1	2	3	4	5
		Zuunbayan oil									
1	Molecular mass	1417	1415	1287	1334	1423	2228	2220	2394	2375	2169
2	C, mass %	85.5	86.5	84.8	86.4	85.2	87.8	86.5	87.2	87.4	88.0
3	H, mass %	8.9	9.0	9.0	9.3	9.3	10.1	10.0	10.2	10.0	9.9
4	N, mass %	1.0	1.0	1.1	1.0	1.0	1.3	1.3	1.2	1.2	1.3
5	S, mass %	0.0	0.0	0.0	0.0	0.0	0.0	1.4	0.0	0.0	0.0
6	O, mass %	4.5	3.4	5.0	3.6	4.5	0.7	0.7	1.3	1..3	0.7
7	C aromatic, %	41.6	43.1	40.7	40.6	40.6	33.7	34.4	35.6	33.5	37.7
8	C naphtene, %	10.9	9.8	11.0	14.6	11.9	24.5	21.9	22.4	26.0	18.9
9	C aliphatic, %	46.5	47.1	48.4	44.8	47.5	41.7	43.8	42.0	39.3	43.4
10	C-α, %	12.9	13.7	14.3	12.5	13.9	12.9	13.1	12.1	13.9	13.8
11	C-γ, %	5.0	3.9	4.4	3.1	4.0	6.1	6.3	4.6	6.4	6.3
	F	9.6	17.3	7.4	17.1	6.8	2.5	9.1	13.1	3.5	4.6
		Usinsk oil									
1	Molecular mass	730	780	886	898	966	1482	1534	1510	1474	1663
2	C, mass %	80.5	81.5	81.3	82.9	82.0	85.8	82.9	85.0	83.9	83.7
3	H, mass %	8.7	8.4	8.1	8.4	8.2	9.0	8.9	8.8	8.8	8.7
4	N, mass %	1.9	1.8	1.6	1.6	1.4	1.9	1.8	1.9	1.9	1.7
5	S, mass %	4.4	4.1	3.6	3.6	3.3	2.2	4.2	4.2	2.2	3.8
6	O, mass %	4.4	4.1	5.4	3.6	5.0	1.1	2.1	1.1	2.2	1.9
7	C aromatic, %	40.8	45.3	48.3	46.8	48.5	49.1	49.1	49.5	53.4	50.9
8	C naphtene, %	12.2	11.3	5.0	9.7	10.6	0.0	0.0	0.0	0.0	0.0
9	C aliphatic, %	46.9	43.4	43.3	43.5	40.9	50.9	50.9	50.5	46.6	49.1
10	C-α, %	16.3	13.2	11.7	12.9	12.1	13.2	13.2	10.3	13.6	11.2
11	C-γ, %	10.2	9.4	10.0	6.5	7.6	5.7	5.7	4.7	5.8	4.3
	F	15.7	13.6	16.2	38.6	19.6	8.4	6.3	18.1	9.1	15.1

CALCULATION OF THERMODYNAMIC CHARACTERISTICS

The method of molecular mechanics allows one to obtain the data concerning the most stable conformation of a molecule [13], to calculate the steric energy. The present method uses the potential energy functions in order to calculate the values of bond energy, the stretching, bending and torsion energy, as well as the energy of non-bonding (electrostatic, dispersion attraction, repulsion) interaction. Thus, the steric energy of molecular conformation could be determined as the sum of stretching, bending, torsion and non-bonding interaction energy.

Procedure of calculation consists in the determination of the steric energy value for the initial configuration of the molecule under study and the subsequent modifying bond lengths and angles with the use of the iterative computing method up to gaining the conformational minimum.

The molecular mechanics method of could warrantee only determining the local minimum of energy with respect to a preset configuration of the molecule. For determining the most stable configuration of a molecule it is necessary to use the method of molecular dynamics. With the mentioned calculation, the molecule can overcome power barriers with obtaining a much more stable conformation.

The steric energy of the molecules constructed (see Table 3) was minimized using MM2 molecular mechanics method. The calculation of

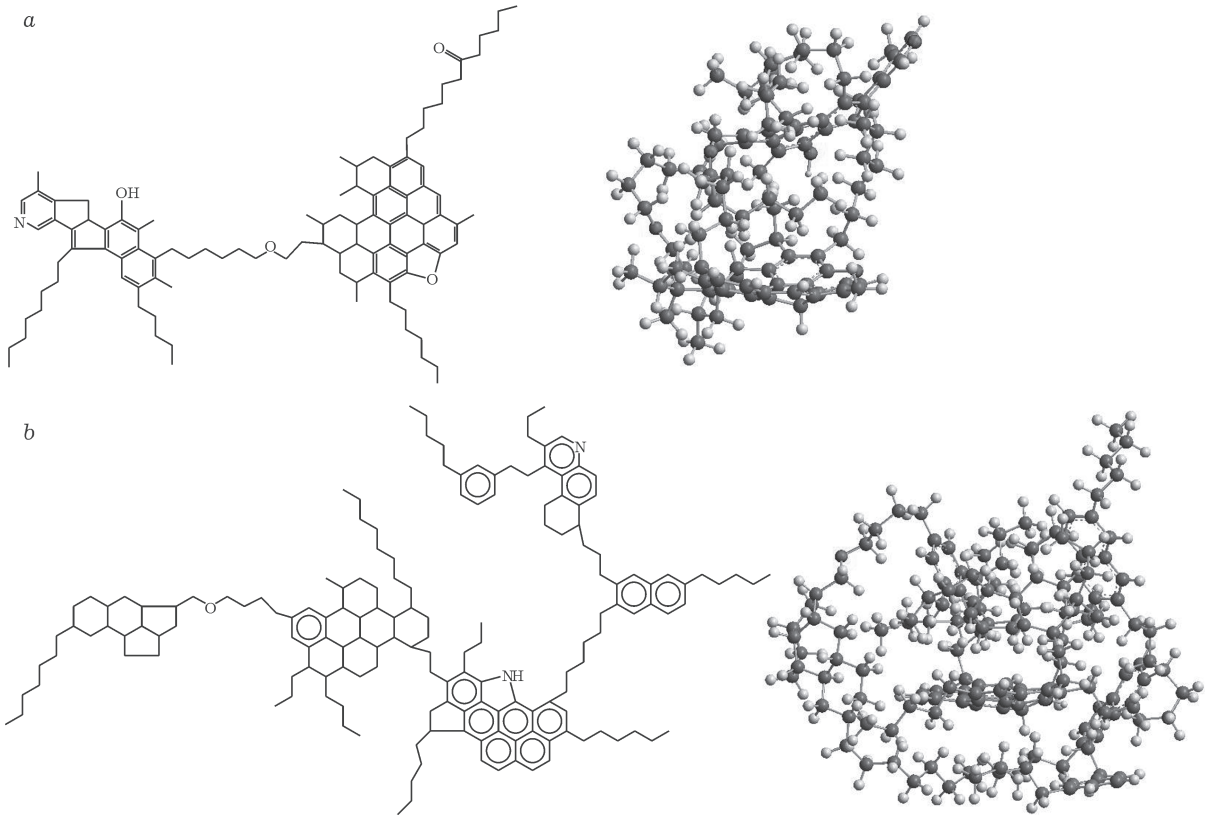

Fig. 4. Spatial structures of molecules No. 5 resins (*a*) and No. 1 asphaltenes (*b*) from the Zuunbayan oil, constructed basing on the program calculations.

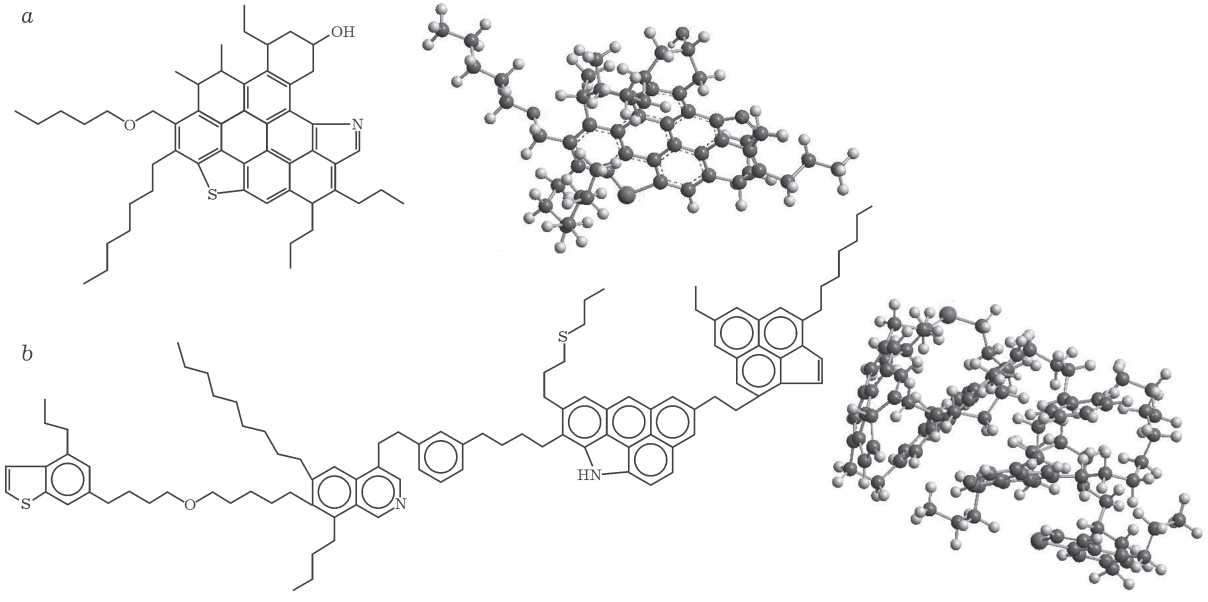

Fig. 5. Spatial structures of molecules No. 2 resins (*a*) and asphaltenes (*b*) from the Usinsk oil, constructed basing on the program calculations.

TABLE 4

Steric energy of the molecules constructed, kcal/mol

Molecule Nos.	Resins	Asphaltenes
	Zuunbayan oil	
1	109.6	93.6
2	120.7	105.8
3	62.5	518.0
4	83.2	153.3
5	87.3	139.7
	Usinsk oil	
1	93.9	99.9
2	64.0	110.4
3	49.8	82.0
4	65.3	47.0
5	51.5	90.1

molecular dynamics was performed for the temperature value of 300 K; the number of iterations was equal to 10 000. The values of molecular steric energy obtained after repeated minimization are presented in Table 4.

The constructed molecules of the Zuunbayan oil resins exhibit a similar structure and identical number of blocks (two). The difference in the steric energy of these molecules is exhibited in the arrangement of the structural blocks of the molecule with respect to each other (Fig. 6). The steric energy of the molecule the is less, the more compactly blocks arranged, the less is the steric energy value.

The minimum energy for the molecules Nos. 3 and 1 of the Usinsk oil resins differs twice amounting to 49.8 and 93.9 kcal/mol, respectively (Fig. 7). Molecule No. 1 consists of one big block whereas molecule No. 3 consists of two structural blocks of a smaller size. To all appearance, just this fact determines so considerable differences in the steric energy of the mentioned structures.

The contribution to the energy minimum of the molecule is made also by the bond length between structural blocks, which influences the spatial structure of the molecule. As demonstrated in Fig. 8, the length of the chain connecting the structural blocks in molecule No. 3 is equal to 10 carbon atoms, whereas molecule No. 1 is linked by less long chains. It should be noted as well, that molecule No.1 consists of six blocks, whereas molecule No. 3 consists of five blocks. The mentioned factors influence the geometry of molecules, the arrangement of its structural blocks and aliphatic chains. One can see that due to the formation of more compact chain packing structure the molecule No. 1 exhibits to a considerable extent lower steric energy as compared to the molecule No. 3.

Just as in the case of resins, the architecture of asphaltene molecules determines the energy parameters. Figure 9 demonstrates the spatial structure of the molecule No. 4 that exhibit a distinct chain packing arrangement with aliphatic chains located on the perimeter. On the contrary, the molecule No. 2 has an opened structure, which results in a considerable difference in the energy minimum state.

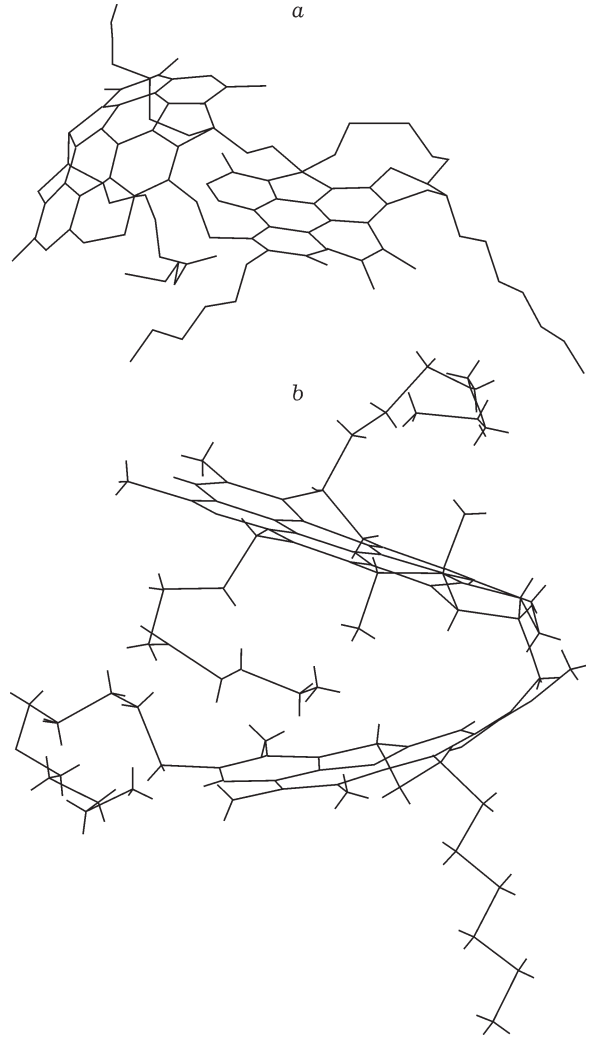

Fig. 6. Molecules Nos. 2 (*a*) and 3 (*b*) of resins from the Zuunbayan oil with the steric energy of 120.7 and 62.5 kcal/mol, respectively.

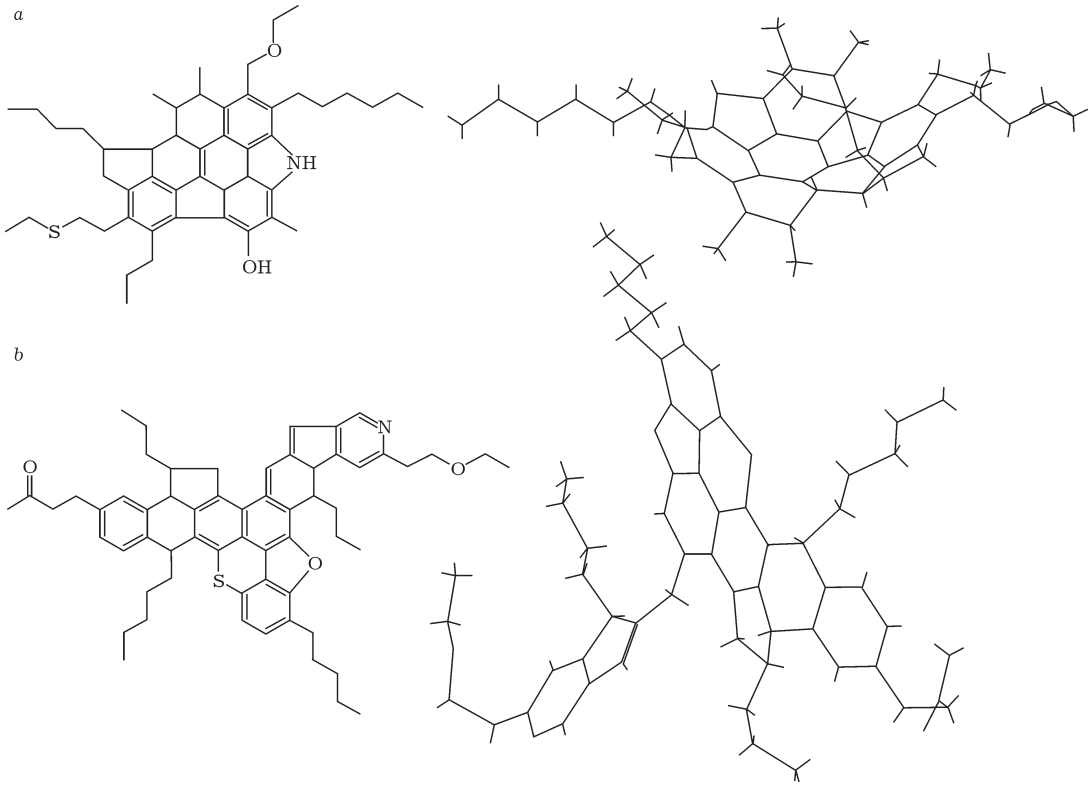

Fig. 7. Molecules Nos. 1 (*a*) and 3 (*b*) of resins from the Usinsk oil with the steric energy of 93.9 and 49.8 kcal/mol, respectively.

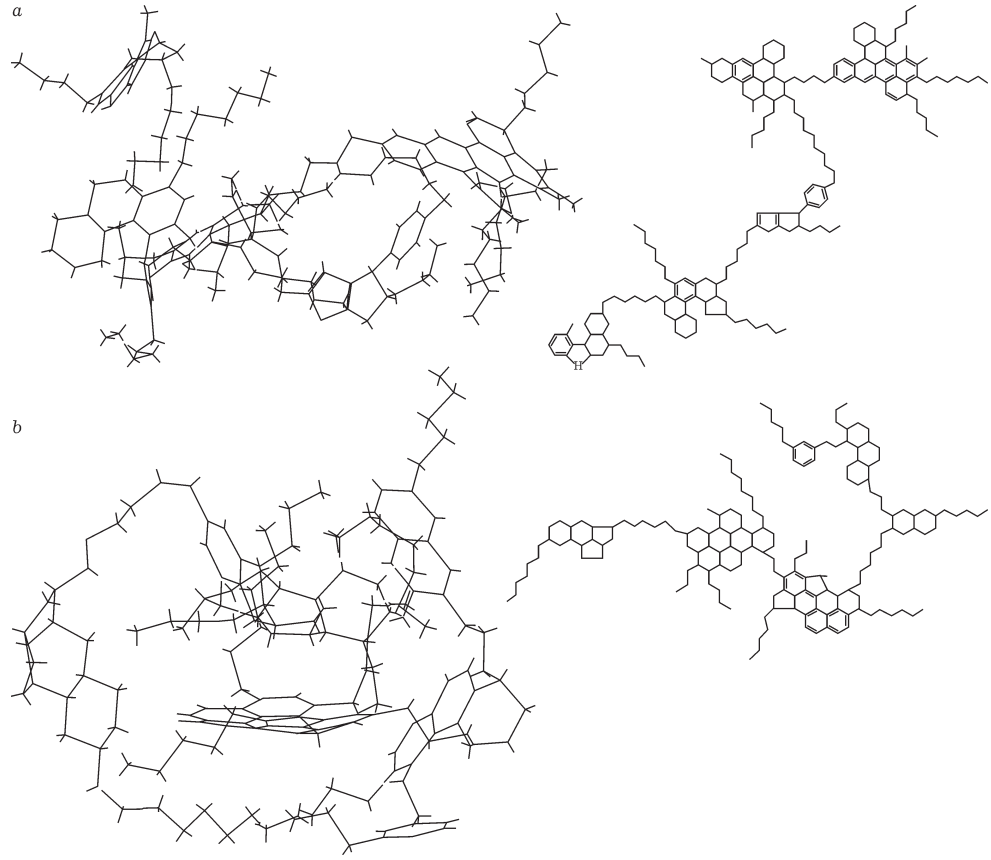

Fig. 8. Molecules Nos. 3 (*a*) and 1 (*b*) of asphaltenes from the Zuunbayan oil with the steric energy of 518.0 and 93.6 kcal/mol, respectively.

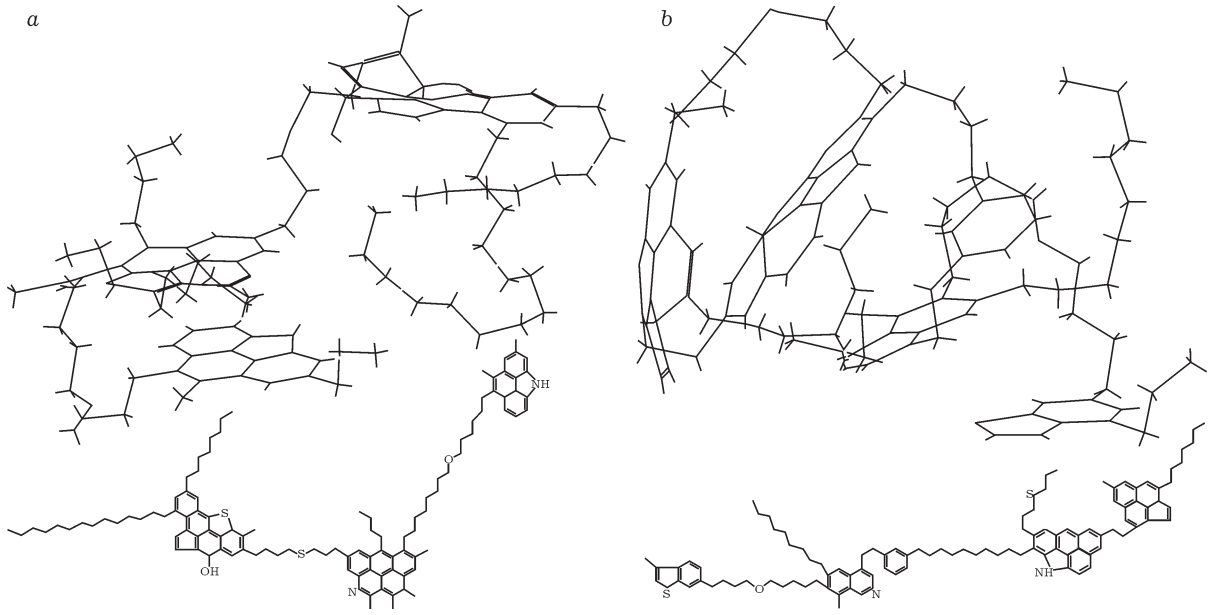

Fig. 9. Spatial structures of molecule Nos. 2 (*a*) and 4 (*b*) of pyrobitumen from the Usinsk oil with the steric energy of 110.4 and 47.0 kcal/mol, respectively.

CONCLUSION

Software is developed that allows modelling the spatial structures of high-molecular compounds formed by resins and asphaltenes of oil and others caustobioliths. The present structural construction could be used for two-dimensional and spatial imaging of molecules and the subsequent calculation of their thermodynamic characteristics by means of the molecular mechanics method or semiempirical calculation methods. The approach proposed for studying high-molecular compounds could be used in combination with experimental data as an additional tool for studying petroleum resins and asphaltenes and their behaviour in various processes.

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