

## CHARACTERIZATION OF HEAVY CRUDE OIL FRACTIONS BY MEANS OF THE $^{13}\text{C}$ -NMR TECHNIQUE

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The  $^{13}\text{C}$ -NMR spectra of samples of heavy crude oil fractions were interpreted. The spectra of all samples were of the same character. In the region of the aliphatic carbon shifts, ten different carbon atom types were discerned; some possible structure types of hydrocarbons were attributed to them and the arrangement of the aromatic rings in a mean molecule of the samples examined was discussed.

The ever-increasing chemical utilization of heavy crude oil fractions calls for a thorough identification of their complex structure. One of the most suitable methods for the structural characterization of these fractions is NMR spectroscopy. Most attention has been devoted to the application of  $^1\text{H}$ -NMR spectroscopy, which yields information on the relative abundances of the various proton types present and by employing appropriate relationships between the hydrogen atoms and the skeleton carbon atoms<sup>1-3</sup> it is possible to calculate the carbon atom distribution within the sample investigated.  $^{13}\text{C}$ -NMR spectroscopy enables a direct study of the carbon atom distribution, its application, however, is hampered by the low magnetic moment of the  $^{13}\text{C}$  isotope and its low natural abundance ( $\sim 1.1\%$ ). Knight<sup>4</sup> combined  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR to structurally characterize aromatic petroleum distillates and Clutter and coworkers<sup>3</sup> to characterize the aromatic fractions isolated from the raw materials for fluid catalytic cracking. A comparison of the potentialities of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR has been demonstrated<sup>5</sup> on a case of analysis of petroleum n-paraffins  $\text{C}_{15}$ — $\text{C}_{20}$ ; the  $^{13}\text{C}$  chemical shifts are up to twenty times more sensitive to the surrounding structure as compared with the proton shifts. The spectra of the corresponding aliphatic and aromatic fractions of different crude oil material displayed identical character, they differed, however, in the relative abundances of the various types of the carbon atoms present<sup>6</sup>. Lindeman and Adams benefited from their experience gained from the  $^{13}\text{C}$ -NMR spectra of paraffins, methylcyclopentanes,

and methylcyclohexanes<sup>7</sup> during the analysis of crude oil distillates with a high content of these compounds<sup>8</sup>. A similar topic was dealt with by Deutsch and coworkers<sup>9</sup>. The most essential contribution of <sup>13</sup>C-NMR spectroscopy to the study of crude oil heavy fractions is the possibility to directly determine the ratio of the number of the aromatic and aliphatic carbon atoms or the ratio of the number of the aromatic carbon atoms to the total carbon atom content, expressed as the coefficient of aromaticity<sup>3,4,10,11</sup>. (The term aliphatic carbon is being used to denote a saturated carbon atom of the alkyl substituents of aromatic rings<sup>1-3</sup>). The accurate value of this ratio can be only obtained in suitable experimental conditions; long relaxation times and the influence of the Overhauser effect on the obtaining of a quantitative <sup>13</sup>C-NMR spectrum call for the application of special experimental techniques<sup>10-13</sup>. In more detail than only to aromatic and aliphatic ones can the carbon atoms be divided only after the comparison with the spectral data of different types of compounds potentially present in the petroleum samples investigated.

Structure analysis of the high-molecular fractions of fossil fuels represents, with regard to their effective exploitation, one of the main tasks of fuel analytical chemistry. In the present work the <sup>13</sup>C-NMR spectra of crude oil heavy fractions are interpreted with the aim to obtain further information on the structure of these samples.

## EXPERIMENTAL

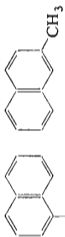

<sup>13</sup>C-NMR spectra were measured on a FT-NMR spectrometer Bruker WP-80 working with quadrature detection with the deuterium internal locking system and broad band decoupler. The samples were measured in 10 mm cells at 30°C, the other parameters were as follows: number of points 8192, pulse width 3 μs (45°C), measured offset 180 ppm, decoupler offset 7-875 ppm, acquisition time 1.092 s, number of FID 3000. The samples of asphalts and atmospheric residues (10% wt.) and of asphaltenes (4-5% wt.) were dissolved in CDCl<sub>3</sub> (Merck). Tetramethylsilane, (Merck) served as the internal standard. The <sup>13</sup>C chemical shifts were read off the spectra obtained with the broad band (noise) decoupling. The shifts of the signals were read off a calibrated paper and rounded to 0.1 ppm.

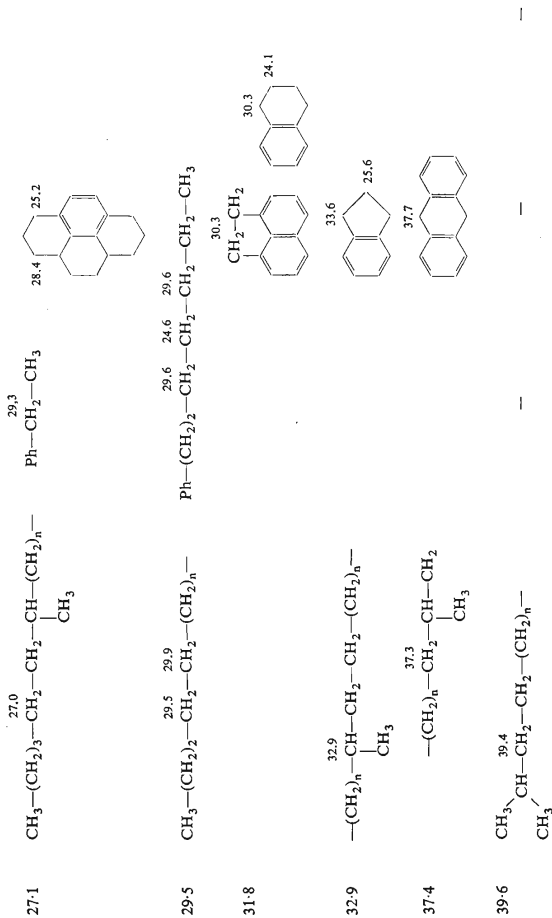
The following samples were subject to analysis: 1) propane asphalt from Romashkino (U.S.S.R.) crude oil, 2) propane asphalt from Saratoff (U.S.S.R.) crude oil, 3) oxidized propane asphalt from Romashkino crude oil, 4) atmospheric residue from West-Siberian crude oil, 5) atmospheric residue from Romashkino crude oil, 6) deasphaltizate of the vacuum residue from Romashkino crude oil, 7) deasphaltizate of the vacuum residue from Arlan (U.S.S.R.) crude oil, 8) asphaltenes from Romashkino crude oil (precipitated with n-pentane), 9) asphaltenes from Saratoff crude oil (precipitated with n-pentane), 10) asphaltenes from the propane asphalt from Saratoff crude oil (precipitated with n-pentane), 11) maltenes from Romashkino crude oil (extracted with n-pentane from propane asphalt of Romashkino crude oil).

## RESULTS AND DISCUSSION

The <sup>13</sup>C-NMR spectra obtained are typical spectra of petroleum samples exhibiting two principal regions (Fig. 1): in the range 13-40 ppm lie the shifts of aliphatic

TABLE I  
 $^{13}\text{C}$  Chemical Shifts in the Aliphatic Region of the Spectra of the Samples Investigated (A) (see Fig. 1), in Long Alkyl Chains (B), and in Alkylaromatic Compounds (C) (Ph = phenyl)

A	B	C
14.1	$\text{CH}_3-(\text{CH}_2)_n-\text{CH}_2-$ 14.1	$\text{Ph}-(\text{CH}_2)_7-\text{CH}_3$ 14.1
19.7	$-(\text{CH}_2)_n-\text{CH}-\text{CH}_3$   $\text{CH}_3$ 19.7	$\text{Ph}-\text{CH}_3$ 21.3  19.1 21.5
22.8	$\text{CH}_3-\text{CH}_2-\text{CH}-(\text{CH}_2)_n$   $\text{CH}_3$ 19.3	
24.6	$-(\text{CH}_2)_n-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_3$   $\text{CH}_3$	$\text{Ph}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ 25.2  25.4 23.0 26.0
24.7	$\text{CH}_3-\text{CH}_2-(\text{CH}_2)_3-(\text{CH}_2)_n-$	



group carbon atoms, in the range 108–150 ppm those of aromatic carbon atoms. Identification of the groups by means of the offset decoupling failed due to the loss in the resolution resulting from the presence of a large quantity of different individual carbon atom types, paramagnetic ions<sup>12</sup>, and free radicals<sup>14</sup> in a mean molecule.

The signals of the aromatic carbon atoms form an envelope; in the region of the aliphatic carbon atom signals, ten types of carbon atoms could be discerned on the envelope. The most intense signal is that belonging to the carbon atoms in the various methylene groups (24.6–29.6 ppm), considerably lower is the proportion of the other aliphatic carbon atoms. The signals of the naphthene carbon atoms could not be directly identified in the spectra of the substances under study. In Table I, some structural types of hydrocarbons are attributed to the chemical shifts of the aliphatic carbon atoms of the samples<sup>15–17</sup>. From the table it follows that in the case of a relatively high content of aromatic carbon atoms in a mean molecule the aromatic ring substituents are probably shorter alkyls ( $n < 5$ ), whereas when the content of the aliphatic carbon atoms is higher, long alkyl chains ( $n > 5$ ) are probably the substituents.

For the sample No 4 featuring a relatively low content of aromatic carbon  $C_{ar}$  23.7% (ref.<sup>12</sup>), three limiting structural models (*I–III*) can be suggested assuming the presence for instance of three aromatic rings in a mean molecule. These models express, based on the elucidation of the <sup>13</sup>C-NMR spectra, the feasible connections

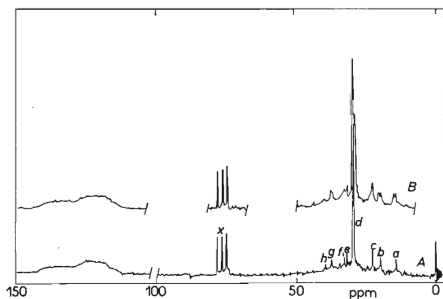
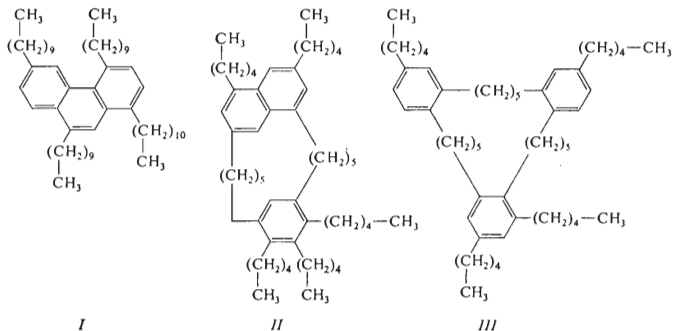


FIG. 1

<sup>13</sup>C-NMR Spectrum of the Atmospheric Residue from West-Siberian Crude Oil

The region 108–150 ppm 5× expanded; for the assignment of the signals *a–j* see Table I; × signal of  $CDCl_3$ ; *A* measured with the broad band decoupling, *B* measured with the offset decoupling.

of the aromatic rings, not reflecting, of course, the presence of heteroatoms and all possible combinations of the alkyl chain arrangements (*i.e.* the mutual lengths of the interbonding and terminal alkyls and their positions).



The structural models shown document the current problems associated with the characterization of the aromatic ring arrangement in a mean molecule of the high-molecular fractions of fossil fuels. The classical conceptions are based on the hypothesis of a highly polycyclic aromatic structure approximated by the model *I* (ref.<sup>18</sup>). This conception makes it possible to calculate the significant structural parameters from the <sup>1</sup>H-NMR data (*e.g.*, the coefficient of aromaticity, total number of the aromatic rings, proportion of alkyls in a mean molecule, *etc.*<sup>1-3</sup>). Recently the possibility of a greater number of smaller interconnected groupings of condensed aromatic rings, as approximated by the models *II* and *III*, has been discussed, particularly for coal samples<sup>19,20</sup>.

From the results of the present work it follows that <sup>13</sup>C-NMR spectroscopy cannot yield sufficient information necessary for the solution of this fundamental problem of fuel structure.

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