

Solid-State NMR Spectroscopy of Ostrava-Karviná Coals

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¹³C CP/MAS NMR structural parameters of Ostrava-Karviná coals were determined. On this basis their aromatic structures were expressed and discussed. It was found that representative structures of Czech bituminous coals are the clusters with 2–4 aromatic rings (mainly 3–4), 1–2 OH groups (mainly 1), and side cycles (six-membered cyclanes or six-membered oxygen-containing heterocyclanes) with quaternary carbons. The cluster size depends on aromaticity of coal.

In the last two decades ¹³C solid-state NMR spectroscopy has been used in the structural analysis of solid fossil fuels and soils. By the use of cross-polarization (CP), magic-angle-spinning (MAS), and dipolar-decoupling techniques, the measurements of the fractions of aromatic and aliphatic/cyclanic carbons, amounts of protonated and nonprotonated carbons and carbon structural distributions were carried out [1, 2]. The dipolar-dephasing (DD) technique along with the normal CP/MAS integrations over selected chemical shift ranges was used to subdivide the fraction of aromatic carbons into the amount of protonated and nonprotonated carbons [2–4]. *Sethi et al.* [5] have demonstrated that a quantitative representation of carbon types can be obtained in such a complicated aromatic structure as it exists in anthracites.

The aim of this work is to determine ¹³C CP/MAS NMR structural parameters of Ostrava-Karviná coals by the use of combination of DD with the CP/MAS integration techniques, to describe their carbon structures and to express representative aromatic units – clusters.

EXPERIMENTAL

As samples, the solid separates obtained from four bituminous coals were used. Powdered coals from Ostrava-Karviná District mines (9. Květen Mine – coals K5 and K7, Fučík Mine – coal F, and Dukla Mine – coal D) were mixed with xylene/tetrachloromethane mixtures (densities of 1.21–1.50 g cm⁻³) and separated into parts with different apparent densities (Table 1) by continuous centrifugation (YEB 1330 and IPB 303 Alfa Laval centrifuges). 10 separates with

low ash and moisture content (0.4–2.9 mass % and 1.5–2.3 mass %, respectively) and with different aromaticity were chosen. Ultimate (elemental) analyses of coal substance of separates obtained are presented in Table 1.

¹³C CP/MAS NMR spectra were measured with the spectrometer Bruker DSX 200 in 7 mm ZrO₂ rotor at the frequencies of 50.33 MHz and 200.14 MHz (¹³C and ¹H, respectively). Number of data points was 0.5 K, magic angle spinning frequency 5.0 kHz, “strength” of *B*₁ field (¹H and ¹³C) was 50.0 kHz. The number of scans for the accumulation of ¹³C CP/MAS NMR spectra was 3600–7200, repetition delay 3 s, and spin lock pulse 1 ms. During the detection a high power dipolar-decoupling was used to eliminate strong heteronuclear dipolar coupling. ¹³C scale was calibrated by external standard glycine ($\delta = 176.03$ – low-field carbonyl signal). For ¹H–¹³C dipolar-dephasing experiments standard pulse sequence was used where cross-polarization period was followed after τ delay by two simultaneous π pulses on both (¹³C and ¹H) channels. Data acquisition starts after another τ delay. 2τ delay was incremented from 2 to 200 μ s. 24 increments were performed to obtain the dipolar-dephasing dependence. The number of scans amounted to 400.

RESULTS AND DISCUSSION

Qualitative and quantitative analysis of ¹³C CP/MAS NMR spectra and ¹³C–¹H dipolar-dephasing experiments were performed. In the ¹³C CP/MAS NMR spectra (Fig. 1) we observed two low intensive spinning side bands SSB-Ar and SSB-Al corresponding to central signals of aromatic and

Table 1. Ultimate (Elemental) Analyses of Coal Substance of the Separates Obtained

Sample	ρ	$w_i/\%$				
	g cm^{-3}	H	C	S	N	O
1	K 5 1.21—1.24	5.9	87.8	0.4	1.3	4.6
2	K 5 1.24—1.27	5.1	87.5	0.3	1.4	5.7
3	K 5 1.27—1.33	4.8	88.5	0.4	1.3	5.0
4	K 5 1.33—1.45	4.5	87.9	0.2	1.2	6.2
5	K 7 1.24—1.27	5.5	86.4	0.3	1.4	6.4
6	K 7 1.31—1.33	5.2	86.4	0.3	1.4	6.4
7	K 7 1.33—1.45	5.1	86.4	0.3	1.3	6.9
8	F 1.27—1.29	5.4	84.2	0.4	1.7	8.3
9	F 1.33—1.45	5.1	84.5	0.5	1.5	8.4
10	D 1.27—1.33	5.0	82.8	0.7	1.5	10.0

ρ – apparent density of the coal separate.

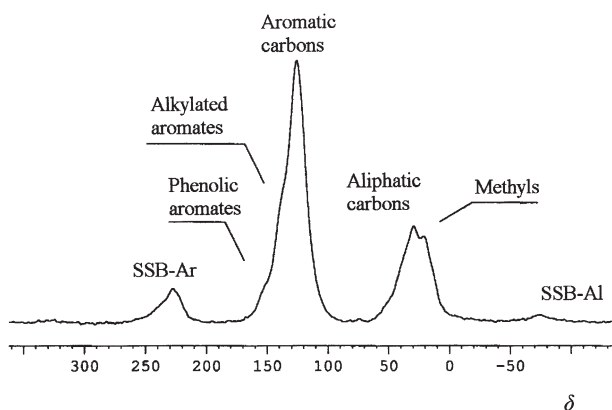


Fig. 1. Typical ^{13}C CP/MAS NMR spectrum of coal separates.

aliphatic/cyclanic structure units, respectively. In the spectra a very weak signal of carbonyl carbons was observed. The content of carbonyls was very low, below 0.6 %. Fraction of aromatic carbons – aromaticity f_a – was calculated from the integral intensity of signals (I_i) according to the following equation

$$f_a = \frac{2I_{\text{SSB-Ar}} + I_{\text{Ar}} - I_{\text{SSB-Al}}}{I_{\text{SSB-Ar}} + I_{\text{Ar}} + I_{\text{Al}} + I_{\text{SSB-Al}}} \quad (1)$$

We supposed the same intensity of ± 1 spinning side bands SSB-Ar and SSB-Al, although the right-hand side SSB-Ar and the left-hand side SSB-Al are overlapped by central signals of aliphatic/cyclanic and aromatics structure units, respectively.

As it follows from [2], the aromatic signal ($\delta = 90\text{--}170$) can be divided into protonated f_a^{H} and non-protonated f_a^{N} carbon fractions according to a portion of Gaussian and Lorentzian magnetization decay measured by $^1\text{H}\text{--}^{13}\text{C}$ dipolar-dephasing experiments

$$f_a^{\text{H}} = f_a M_{0\text{G}} \quad (2)$$

$$f_a^{\text{N}} = f_a M_{0\text{L}} \quad (3)$$

$M_{0\text{G}}$ and $M_{0\text{L}}$ – initial magnetizations – were calculated by fitting of experimentally determined dipolar-dephasing dependences (Fig. 2a) according to the equation describing mixed Lorentzian and Gaussian carbon magnetization decay

$$M = M_{0\text{L}} \exp\left(-\frac{t}{T_{\text{L}}}\right) + M_{0\text{G}} \exp\left(-\frac{t}{T_{\text{G}}}\right) \quad (4)$$

The dipolar-dephasing decay time constants T_{G} and T_{L} (Gaussian and Lorentzian, respectively) and the initial magnetizations are summarized for aromatic as well as aliphatic/cyclanic carbon signals in Table 2 (the samples in Tables 2–4 are ranged by decreasing aromaticity f_a , see Table 3). Strongly coupled aromatic carbons with Gaussian magnetization decay (protonated carbons) have decay time constants in a narrow range from 26 to 32 μs and account for about 51–61 % (initial magnetization intensity $M_{0\text{G}}$). Aromatic weakly coupled carbons with Lorentzian magnetization decay (nonprotonated carbons) have decay time constants that range from 137 to 268.5 μs and

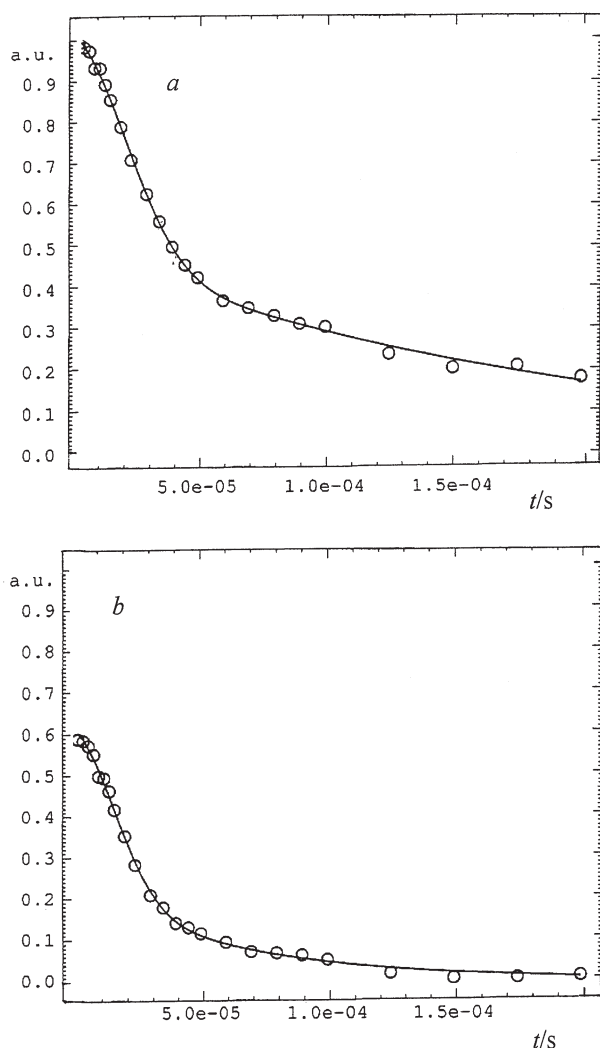


Fig. 2. Dipolar-dephasing magnetization decay of aromatic signal (a) and aliphatic signal (b).

their fraction is between 39—49 % of initial magnetization intensity M_{0L} .

The signal of nonprotonated aromatic carbons can

be further decomposed into the three components. Signals of phenolic carbons are in the range of chemical shift δ from 150 to 165. Alkylated aromatic carbons resonate at $\delta = 135$ —150. Signals of bridgehead carbons fall in the range of chemical shift lower than $\delta = 135$. To determine the fraction of the above-mentioned carbons, the signal of aromatics was deconvoluted into three components. One component, which is reflected by a shoulder at $\delta \approx 150$ reflects the phenolic carbons fraction f_a^P . The second component (shoulder at $\delta \approx 140$) corresponds to the fraction of alkylated aromatic carbons f_a^S . Both these fractions f_a^P and f_a^S can be directly determined by the decomposition of the aromatic signal (Fig. 3a). The fraction of bridgehead carbons f_a^B was obtained by subtracting the fraction of phenolic and alkylated aromatic carbons from the fraction of nonprotonated aromatic carbons

$$f_a^B = f_a - f_a^P - f_a^S \quad (5)$$

Aliphatic/cyclanic signal with a chemical shift at $\delta = 10$ —50 was decomposed into two main components according to magnetization behaviour during ^1H — ^{13}C dipolar-dephasing experiments (Fig. 2b) similarly as in the case of an aromatic signal. At first, Gaussian magnetization decay reflects strongly proton-coupled aliphatic/cyclanic carbons (CH and CH_2). Fraction of protonated aliphatic/cyclanic carbons f_{al}^H is to be calculated by

$$f_{al}^H = f_{al} M_{0G} \quad (6)$$

where f_{al} is a fraction of aliphatic/cyclanic carbons ($f_{al} = 1.00 - f_a$). Magnetization decay of strongly coupled carbons is described by the decay time constants ranging from 23 to 26 μs with a fraction of about 45—73 % (initial magnetization intensity, Table 2). The Lorentzian magnetization decay then corresponds with weakly proton-coupled carbons such as methyl and/or quaternary carbons. Their fraction f_{al}^N is calculated as

$$f_{al}^N = f_{al} M_{0L} \quad (7)$$

Table 2. Dipolar-Dephasing Decay Time Constants T_G and T_L and Initial Magnetizations M_{0G} and M_{0L}

Sample	Aromatic carbons				Aliphatic carbons			
	$T_L/\mu\text{s}$	$T_G/\mu\text{s}$	M_{0L}	M_{0G}	$T_L/\mu\text{s}$	$T_G/\mu\text{s}$	M_{0L}	M_{0G}
4	137.1	29.1	0.47	0.53	45.6	24.1	0.55	0.45
7	183.1	31.4	0.47	0.53	79.3	26.1	0.28	0.72
3	195.5	29.6	0.42	0.58	67.1	25.6	0.36	0.64
2	268.5	31.9	0.39	0.61	72.5	26.1	0.40	0.60
1	189.2	30.7	0.48	0.52	63.4	24.7	0.37	0.63
6	181.4	29.4	0.44	0.56	62.9	24.9	0.32	0.68
9	186.4	30.6	0.49	0.51	58.8	23.4	0.39	0.61
5	197.4	31.1	0.46	0.54	59.4	23.6	0.40	0.60
8	200.1	30.9	0.41	0.59	70.1	25.4	0.27	0.73
10	136.7	26.4	0.44	0.56	44.0	24.3	0.35	0.65

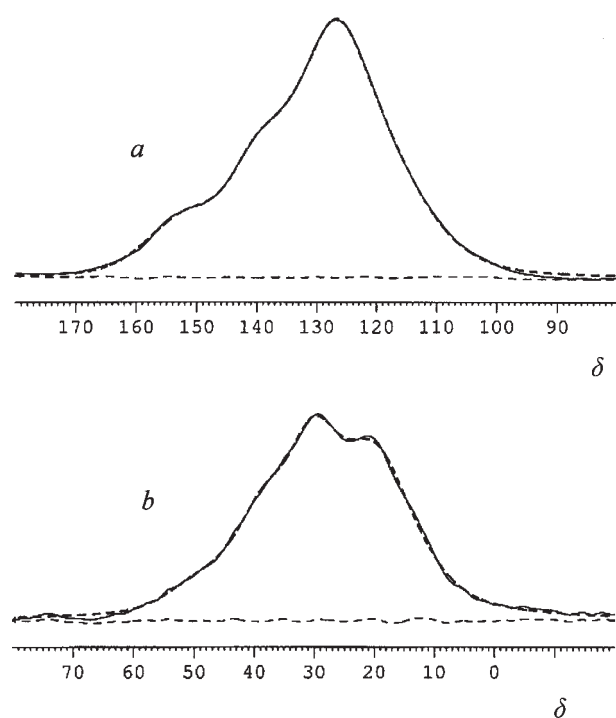


Fig. 3. Deconvolution of aromatic (a) and aliphatic (b) signal. Solid line – experimental, thick dashed line – overall signal after deconvolution, thin dashed line – subtraction of experimental and simulated spectra.

The decay time constants in this region vary from 46 to 79 μs with initial magnetization intensity 27–55 % for weakly coupled aliphatic/cyclanic carbons (Table 2).

A higher fraction of strongly coupled carbons (aliphatic/cyclanic as well as aromatic) was found in nearly all samples. Aliphatic/cyclanic carbons attached to oxygen resonate at $\delta = 50$ –90, however, the fraction of such carbons could not be directly determined by decomposition of the aliphatic/cyclanic

carbons signal because only a small shoulder in this region was observed.

As it followed from the ^1H – ^{13}C dipolar-dephasing experiments, the two main signals at $\delta = 29$ and 21 exist in the region $\delta = 10$ –50. These signals reflect differently dipolar coupled carbons to protons in groups. A much faster decay of the signal at $\delta = 29$ then corresponds with strongly dipolar coupled carbons (CH_2 and CH) contrary to slower magnetization decay of weakly coupled aliphatic/cyclanic carbons with the signal at $\delta = 21$ (mainly CH_3). Fraction of methyl carbons f_{al}^{M} was then directly determined by decomposition of the signal (Fig. 3b). By subtraction from f_{al}^{N} , the fraction of quaternary carbons f_{al}^{Q} was calculated. All determined values of the above-mentioned fractions are summarized in Table 3.

As the amount of bridgehead carbons f_{a}^{B} generally increases with the increasing aromaticity f_{a} , the mole fraction of aromatic bridgehead carbons calculated as $\chi_{\text{B}} = f_{\text{a}}^{\text{B}}/f_{\text{a}}$ can be used to estimate the size of the aromatic cluster (aromatic-cyclanic unit in coal macromolecular network) as the number of aromatic carbon atoms per cluster. The basic model of relationship of χ_{B} to the structure of polycondensed aromatic clusters was well defined and described [2]. According to the equation

$$\chi_{\text{B}} = \frac{1 - \tanh\left(\frac{C - C_0}{m}\right)}{2} \left(\frac{1}{2} - \frac{3}{C}\right) + \frac{1 + \tanh\left(\frac{C - C_0}{m}\right)}{2} \left(1 - \frac{\sqrt{6}}{\sqrt{C}}\right) \quad (8)$$

where C is the number of aromatic carbon atoms per aromatic cluster and C_0 and m are adjustable parameters, one can determine the number of carbons C in an aromatic cluster. The values of adjustable param-

Table 3. Fractions of Carbons (Distribution of Structural Carbons)

Sample	f_{a}	f_{a}^{H}	f_{a}^{N}	f_{a}^{P}	f_{a}^{S}	f_{a}^{B}	f_{al}	f_{al}^{H}	f_{al}^{N}	f_{al}^{M}	f_{al}^{Q}
4	0.78	0.41	0.37	0.07	0.04	0.26	0.22	0.10	0.12	0.03	0.09
7	0.77	0.41	0.36	0.07	0.05	0.24	0.23	0.16	0.07	0.02	0.05
3	0.76	0.44	0.32	0.06	0.04	0.22	0.24	0.15	0.09	0.04	0.05
2	0.76	0.46	0.30	0.05	0.05	0.20	0.26	0.16	0.10	0.05	0.05
1	0.74	0.39	0.35	0.05	0.08	0.22	0.26	0.16	0.10	0.05	0.05
6	0.73	0.41	0.32	0.04	0.07	0.21	0.27	0.18	0.09	0.04	0.05
9	0.71	0.36	0.35	0.10	0.06	0.19	0.29	0.18	0.11	0.06	0.05
5	0.71	0.38	0.33	0.09	0.06	0.18	0.29	0.18	0.11	0.06	0.05
8	0.67	0.40	0.27	0.05	0.08	0.14	0.33	0.24	0.09	0.05	0.04
10	0.64	0.34	0.30	0.07	0.09	0.14	0.36	0.23	0.13	0.13	0.00

f_{a} – aromaticity; f_{a}^{H} – fraction of protonated aromatic carbons; f_{a}^{N} – fraction of nonprotonated aromatic carbons; f_{a}^{P} – fraction of phenol aromatic carbons; f_{a}^{S} – fraction of alkylated aromatic carbons; f_{a}^{B} – fraction of bridgehead aromatic carbons; f_{al} – fraction of aliphatic/cyclanic carbons; f_{al}^{H} – fraction of protonated aliphatic/cyclanic carbons (CH , CH_2); f_{al}^{N} – fraction of nonprotonated aliphatic/cyclanic carbons (C , CH_3); f_{al}^{M} – fraction of CH_3 carbons; f_{al}^{Q} – fraction of quaternary carbons.

Table 4. Numbers of Carbons (Types of Structural Carbons) per Cluster

Sample	χ_B	C	C_a^H	C_a^N	C_a^P	C_a^S	C_a^B	C_{att}	C_{al}	C_{al}^H	C_{al}^N	C_{al}^M	C_{al}^Q
4	0.325	16	8.4	7.6	1.4	0.8	5.3	2.2	4.5	2.1	2.4	0.6	1.8
7	0.31	15	8.0	7.0	1.4	1.0	4.6	2.3	4.5	3.1	1.4	0.4	1.0
3	0.29	14	8.1	5.9	1.1	0.7	4.1	1.8	4.4	2.8	1.6	0.7	0.9
2	0.26	13	7.8	5.2	0.9	0.9	3.4	1.7	4.4	2.7	1.7	0.8	0.9
1	0.29	14	7.4	6.6	0.9	1.5	4.2	2.5	4.9	3.0	1.9	0.9	1.0
6	0.29	14	7.8	6.2	0.8	1.3	4.1	2.1	5.2	3.4	1.8	0.8	1.0
9	0.27	13	6.6	6.4	1.8	1.1	3.5	2.9	5.3	3.3	2.0	1.1	0.9
5	0.25	12	6.4	5.6	1.5	1.0	3.1	2.5	4.9	3.0	1.9	1.1	0.8
8	0.20	10	6.1	3.9	0.8	1.1	2.0	1.9	4.9	3.6	1.3	0.7	0.6
10	0.22	11	5.8	5.2	1.2	1.6	2.4	2.8	6.2	4.0	2.2	2.2	0.0

χ_B – the mole fraction of aromatic bridgehead carbons. $C_a^i = (f_a^i/f_a)C$; $C_{al}^i = (f_{al}^i/f_{al})C_{al}$, where C_{al} was calculated from $f_{al} = C_{al}/(C_{al} + C)$. C – number of aromatic carbons; C_a^H – number of protonated aromatic carbons; C_a^N – number of nonprotonated aromatic carbons; C_a^P – number of phenol aromatic carbons; C_a^S – number of alkylated aromatic carbons; C_a^B – number of bridgehead aromatic carbons; C_{att} – number of attachments; C_{al} – number of aliphatic/cyclanic carbons; C_{al}^H – number of protonated aliphatic/cyclanic carbons (CH, CH₂); C_{al}^N – number of nonprotonated aliphatic/cyclanic carbons (C, CH₃); C_{al}^M – number of CH₃ carbons; C_{al}^Q – number of quaternary carbons; all per cluster.

eters were $C_0 = 19.57$ and $m = 4.15$. The number of attachments per cluster can be defined as

$$C_{att} = C \frac{f_a^S + f_a^P}{f_a} \quad (9)$$

The calculated ¹³C CP/MAS NMR parameters, χ_B and the numbers of carbon atoms per aromatic cluster C_i are listed in Table 4.

On the basis of all calculated structural parameters we proposed the representative clusters of coal samples (Fig. 4). One should take into account that every coal sample represents a mixture of wide series of different cyclanic-aromatic clusters, and the distribution of these clusters determines resulting structural parameters obtained by ¹³C CP/MAS NMR experiments. Therefore, the calculated parameters are only average values.

In the coal structure oxygen plays an important role. Because aryl alkyl ethers and diaryl ethers were identified and quantified by the DRIFTS-PLS method in the studied separates [6], ethereal oxygen was included in presented structures. In the case of coal, structure units containing other heteroatoms (S, N) are in minority or negligible. Therefore, from hetero compounds the oxygenized structures were considered only. Structures of representative clusters in Fig. 4 prove that in Czech bituminous coals the clusters with 2—4 aromatic rings (mainly 3—4), 1—2 OH groups (mainly 1), and side cycles (six-membered cyclanes or oxygen-containing heterocyclanes) with quaternary carbon exist in coal macromolecular network as prevailing form of condensed aromatics. The cluster size depends on aromaticity of coal sample. For f_a 0.64, 0.67, and 0.71 the cluster size of two aromatic rings was observed, for f_a 0.71—0.77 of three and for f_a 0.78 of four aromatic rings was found. Presence of condensed aromatic units in coal structure was proved also by the results of hydrogenation

and extraction of coal [7], X-ray photoelectron spectroscopy [8], and atmospheric-pressure temperature-programmed reduction [9] of coal separates.

Wide range of Lorentzian decay time constants for aromatic carbons (Table 2) reflects a huge variability of structure of clusters. This Lorentzian component indicates the strength of ¹H—¹³C dipolar coupling between indirectly coupled nuclei with a relatively large distance within one cluster as well as between neighbouring clusters. Therefore, the packing of clusters also determines this decay time constant. In addition, the dynamics of all clusters can affect this parameter. From this it follows that it is very difficult to extract any additional structural parameter from this constant T_L and to find a simple dependence on the structure of clusters. Only the shortest T_L times (136.7 μ s and 137.1 μ s) for the clusters in the samples 10 and 4, respectively, indicate compact packing of clusters and thus their low mobility, contrary to the other samples. As Gaussian magnetization decay predominantly reflects the strength of dipolar interaction of directly coupled protons to carbons in aromatic rings, we observe a relatively very narrow range of the decay time constants. However, also in this case the shortest values T_G correspond with the mobility of clusters and thus confirm their lower mobility and dense packing in the samples 10 and 4.

Similar characteristic features were also observed for dipolar dephasing decay time constants of aliphatic/cyclanic carbons. Small variation of Gaussian decay time constants, which reflect dipolar interactions in CH and CH₂ groups, indicates that chains are short and probably form cyclanes. With longer and linear side chains one should expect wider variation in dynamic state and from this resulting wider range of decay time constants, which should depend on a fraction of aliphatic/cyclanic carbons. Although the fraction of protonated aliphatic carbons varies from 10 % to 24 %

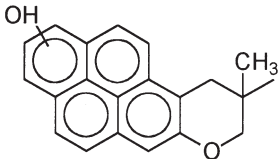
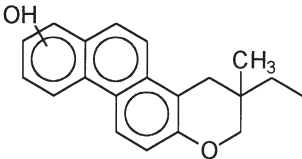
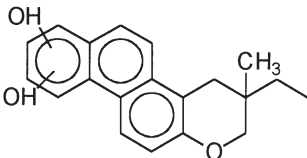
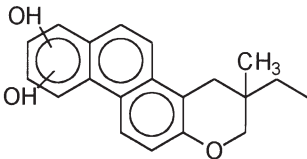
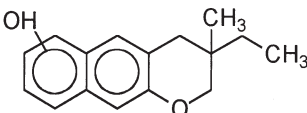
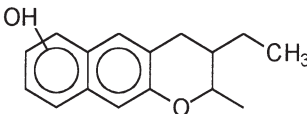
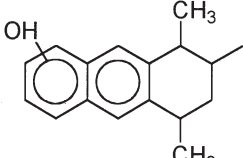
Sample	f_a	Representative structure
4	0.78	
7, 3, 2, 1, 6	0.73—0.77	
9	0.71	
5	0.71	
		
8	0.67	
10	0.64	

Fig. 4. Representative structures (clusters) of Ostrava-Karviná coals.

(Table 3), the T_G time falls in the range from 23.4 μs to 26.1 μs (Table 2). High portion of cyclanes (connected to aromatic rings) is directly confirmed by the calculated number of methyls, quaternary carbons, and CH and CH_2 groups per one aromatic cluster (Table 4).

The magnetization decay of coal sample with the lowest f_a 0.64 (10) is fast with low component of Gaussian decay. Gaussian decay time constant for aromatic carbons is very short (Table 2), in addition, magnetization decay of aromatic carbons shows dipolar oscillation that was not observed in other cases. Such dipolar

oscillation reflects a relatively weak heteronuclear dipolar interaction and can be observed with relatively isolated proton-carbon spin pairs. Effective spin isolation can result from higher mobility or from larger spatial separation of protons. The higher molecular mobility is not probable, so the dipolar oscillation indicates longer average internuclear distance. Because the fraction of protonated aromatic carbons is very low in this case (34 %, Table 3), the proton density within the sample is also low. This results in a longer average proton—carbon distance and ^1H — ^{13}C isolation. Magnetization behaviour of the sample with the lowest f_a (from the Dukla coal) was different in comparison with the other ones.

The presented method can be used to structural characterization of cokes, chars, carbonaceous sorbents, solid caustobioliths, C—C composites, and coal tar pitches. The application to the characterization of solid products of co-pyrolysis of waste plastics and organics with coal is of importance, because in this way these wastes can be converted to useful products [10]. On the basis of works [11—13] the broader use of the described method in the field of organic geochemistry, soil chemistry, and coal-derived products can be considered.

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