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GAS CHROMATOGRAPHY–MASS SPECTROMETRY STUDY OF COAL-DERIVED ASPHALTENES

II. CARBAZOLE-TYPE NEUTRAL NITROGEN COMPOUNDS

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SUMMARY

An approach to the selective determination of carbazole-type neutral nitrogen compounds is suggested. Carbazoles, benzocarbazoles and their alkyl derivatives were obtained as homogeneous fractions after extensive chromatographic separation. The number and the position of alkyl substituents were determined by ^{1}H NMR and mass spectrometry. The following homologous series were found in coal liquefaction asphaltenes: $Z(\mathrm{N}) = -15$, C_{12}–C_{18}; -17, C_{17}, C_{18}, C_{20}; -19, C_{14} and -21, C_{16}–C_{20}. The content of carbazole and its alkyl derivatives was one order of magnitude larger than that of other series.

INTRODUCTION

Nitrogen compounds in coal liquefaction products are present in various chemical forms. Similarly to the group analysis of petroleum, they can be divided into basic, *i.e.*, pyridines, acridines, quinolines and neutral products *i.e.*, pyrroles, carbazoles, amines, nitriles, lactams, etc. Most methods for the characterization of asphaltenes in coal-derived liquids (CDLs) are similar to those applied in the analysis of high-boiling petroleum fractions and residues[1,2], accounting for the specific features of coal asphaltenes.

As a first step in an investigation of nitrogen species their chemical nature should be determined. The present study focuses on neutral nitrogen compounds (NNCs). In contrast to the basics which are readily extractable from the total mixture, the NNCs can be concentrated only to a certain degree. Early studies relied on counter-current extraction and chromatography[3–6]. Recently, Later *et al.*[7–9] developed a scheme whereby the nitrogen compounds are divided into quinoline basics, pyrrole compounds and amines. Using this method, Nashioka *et al.*[10,11] succeeded in identifying compounds with mixed functionalities, *e.g.*, aminobenzothiophenes, hydroxycarbazoles, hydroxyacridines, etc. Heteroatom-containing compounds with three to ten fused aromatic rings were assessed by high-efficiency microcolumn chromatography and fluorescence[12]. Other authors prefer the use of column packings modified by electron-transfer reagents[13].

TABLE I

CHARACTERIZATION OF THE INITIAL SAMPLE

Sample	*Yield of the eluate (%, w/w)*	*Number-average molecular weight determined by osmometry*	*Elemental composition (%, w/w)*				
			C	*H*	*N*	*S*	*O**
I	24.6	350	84.98	10.08	0.74	2.70	1.50
II	30.5	315	89.48	6.63	1.00	1.16	1.73
III	7.7	360	89.36	6.06	1.90	1.33	1.34

* By difference.

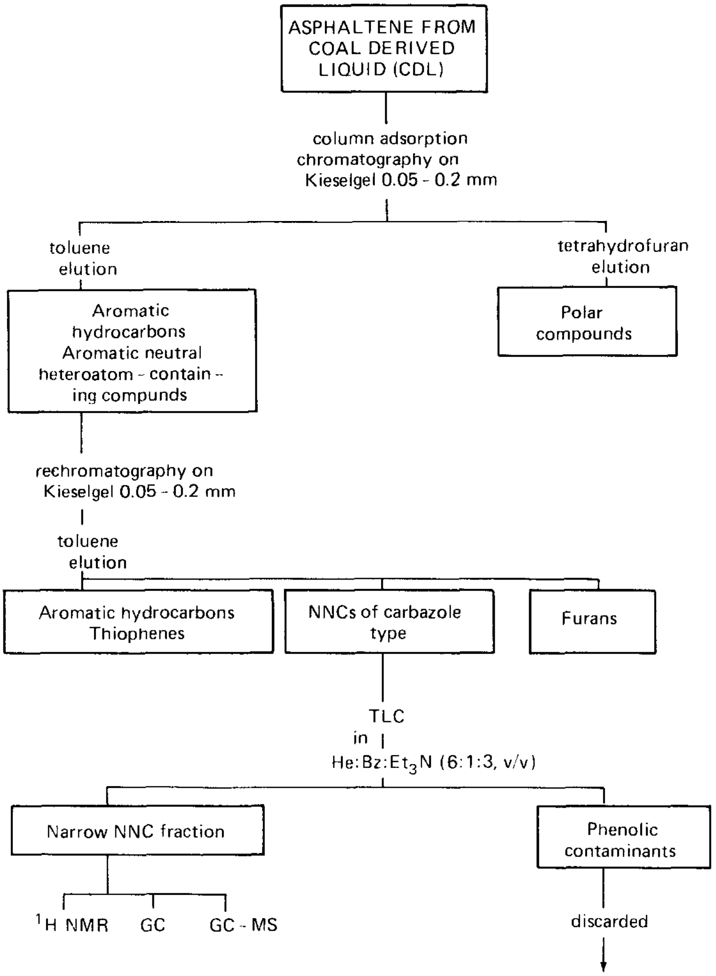
The chromatographic behaviour of variously substituted carbazoles, benzocarbazoles and dibenzocarbazoles was studied in detail and a number of empirical rules for the retention times and positions of the substituents were deduced[14–19].

The aim of the present paper is to establish the chromatographic approach for the selective isolation and further characterization of NNCs of the carbazole type, found in coal liquefaction asphaltenes.

EXPERIMENTAL

The experiments were carried out with asphaltenes from the liquefaction of lignite (carbon content calculated to "dry ash free" basis, C^{daf} = 65.2%), sample I; sub-bituminous coal (C^{daf} = 70.1%), sample II; bituminous coal (C^{daf} = 81.2%), sample III. The column chromatographic fractionation is described in a previous paper[20]. It was considered that the toluene eluate comprised polycyclic aromatic hydrocarbons and their heteroatom-containing analogues of the pyrrole, thiophene and furane types. The characterizations of the eluates are presented in Table I. The analytical fractionation is illustrated in Scheme 1. The toluene eluates were rechromatographed on a silica gel column (900 mm × 7 mm). The adsorbent (Kieselgel, 0.05–0.2 mm; E. Merck, Darmstadt) was activated at 165°C for 2 h. The column was dry-packed. The sample (0.2–0.3 g) was dissolved in 3 ml toluene. The solvent was removed and the sample remained adsorbed on a small part of the silica gel. The adsorbed sample was loaded on the top of the column. The toluene elution was performed under gravity pressure. Fractions of 2 ml were collected. Each was applied as a 0.2% solution on thin-layer plates (Kieselgel 60 F_{254}, 0.25 mm) activated at 120°C for 1 h. The plates were developed by benzene. The functional groups present were identified after spraying with a benzene solution of tetracyanoethylene. Carbazole and its derivatives exhibited a blue-green spot, benzocarbazole a yellow spot. All fractions with positive colour reactions were pooled and subjected to further analysis. Carbazole was obtained from E. Merck. N-Methylcarbazole, 1,4-dimethylcarbazole, 1,4,6,8-tetramethylcarbazole and 3-octadecylcarbazole were synthesized by Frolov *et al.*[21] and together with 3,4-benzocarbazole (benzo[*c*]carbazole) were gifts. The ring numbering used for the carbazole derivatives is in accord with that of Ignatiadis *et al.*[17].

Phenolic compounds sometimes present in the analyzed mixture were eliminated



Scheme 1. Isolation and characterization of NNCs of the carbazole type from coal liquefaction asphaltene. He:Bz:Et_3N = hexane–benzene–triethylamine.

by preparative thin-layer chromatography (TLC) in hexane–benzene–triethylamine (6:1:3, v/v)[21]. Under these conditions the retention of carbazole is twice as low as that of phenols and other contaminants of aromatic hydrocarbons. Following TLC separation, the band with R_F 0.2–0.55 was removed. The narrow carbazole fractions of NNCs (NNC I, II, III, respectively) were characterized by ^1H NMR spectroscopy. The spectra were measured as 10% (w/w) solutions in deuterochloroform and differentiated with respect to tetramethylsilane as an internal standard: H_γ, 0.5–1.0; H_β, 1.0–2.0; H_α, 2.0–3.5; H_{ar}, 6.0–9.0 ppm.

The gas chromatograms were obtained with a Carlo Erba-GC VEGA 6000 instrument, a glass capillary column (25 m × 0.25 mm I.D.) packed with OV-17 (thickness 0.1–0.15 μm) and a flame ionization detector with $t^0_{det.}$ and $t^0_{inj.}$ = 280°C. The temperature was raised from 140 to 260°C at 2°C/min, and then held till the

TABLE II

DISTRIBUTION OF THE PROTONS IN ^1H NMR SPECTRA, IN %

Sample	H_{ar}	H_{α}	H_{β}	H_{γ}
NNC I	30.40	23.40	31.20	15.00
NNC II	33.00	25.50	32.00	9.50
NNC III	32.60	6.50	45.50	15.40

sample was completely volatilized. Chart speed: 0.5 cm/min. The retention times are given in minutes. The identification of individual standards was based on a comparison of retention times on the capillary column of standards and substances. The chromatograms were interpreted quantitatively by a Carlo Erba Model Mega integrator.

For gas chromatography–mass spectrometry (GC-MS), a 25-m OV-101 fused-silica capillary column was used in a JEOL JGC-20K gas chromatograph, directly coupled to a JEOL JMS-D 300 mass spectrometer. The samples were introduced via a metal injector working in split mode, with helium as the carrier gas; temperature range 140–280°C at 2°C/min. The mass spectrometer was operated in the electron-impact mode; ionization potential 70 eV; ionization current 300 μA and ion-source temperature 200°C. The GC investigation of the reference compounds revealed their high purity (>99%), so that they were directly introduced into the ion source.

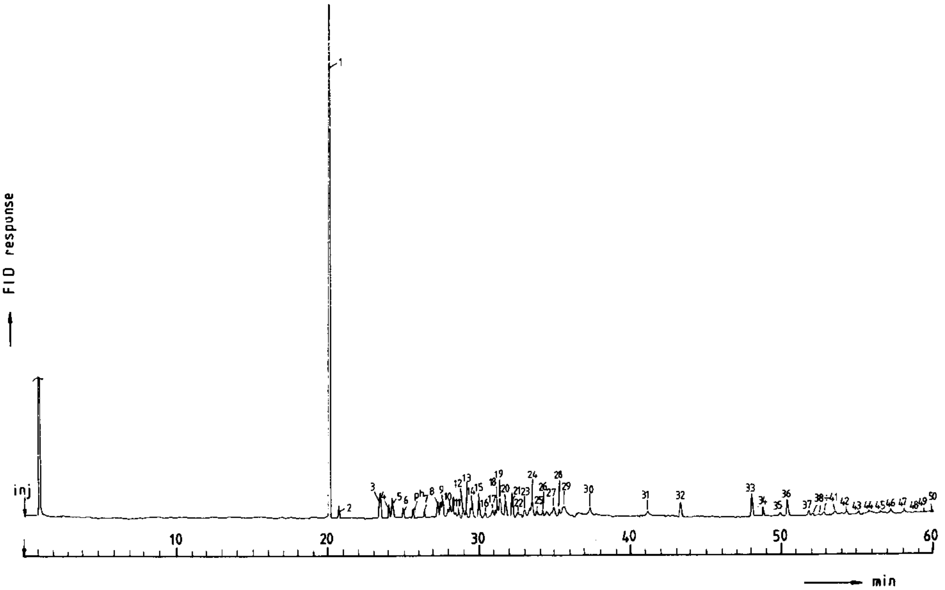


Fig. 1. GC separation of sample NNC I. Conditions: Carlo Erba-GC VEGA 6000 equipped with a Carlo Erba Mega series integrator; glass capillary column coated with OV-17, thickness 0.1–0.15 μm, 25 m × 0.25 mm I.D.; temperature programmed from 140 to 260°C at 2°C/min; flame ionization detection; t^0_{inj} and t^0_{det} 280°C. For peak identification see Table III. ph = Phthalate.

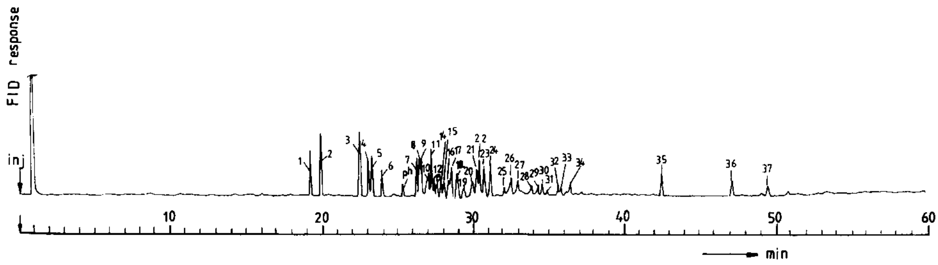


Fig. 2. GC separation of sample NNC II. For peak identification see Table IV.

Compounds were classified according to their Z numbers derived from the molecular weight (MW), obtained by GC–MS, using the general formula $C_nH_{2n+z}N$. $(-Z)N$, $Z = N(-15)$, $Z = N(-17)$, $Z = N(-19)$, $Z = N(-21)$ explain the hydrogen deficit.

RESULTS

Aromatic hydrocarbons are eluted in the first 10 ml in column adsorption chromatography. The next 20 ml (on average ten fractions) yield the colour reaction. About 10–20 mg of the carbazole fraction (NNC I–NNC III) were obtained by chromatography. They constitute 5–7% of the eluate analyzed and less than 1% of the initial asphaltenes. These data are considered as semi-quantitative with respect to the starting sample. Since we were looking for a method for the selective isolation of NNCs

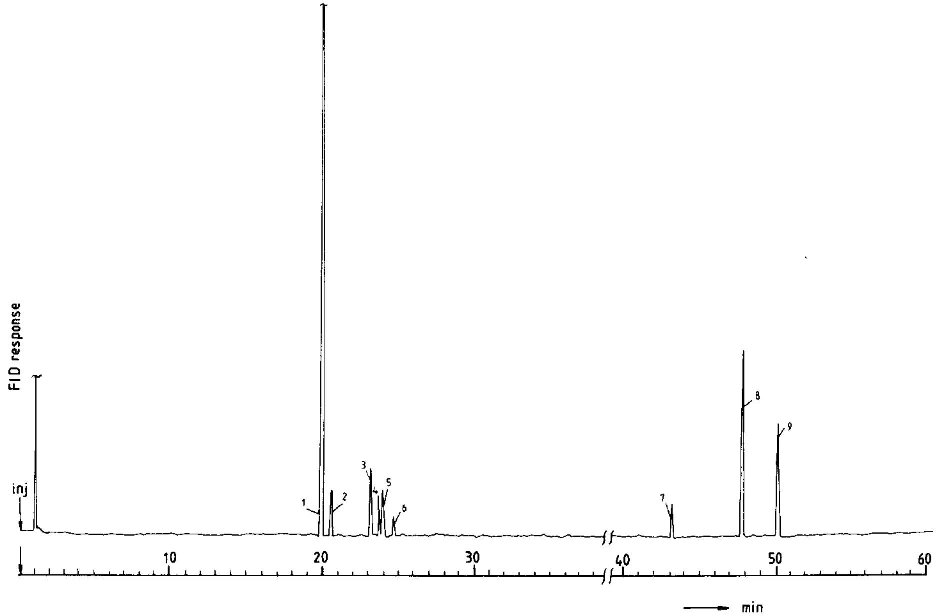


Fig. 3. GC separation of sample NNC III. For peak identification see Table V.

of the carbazole type as an individual fraction with a maximum concentration, a large number of chromatographic steps was necessary, as illustrated in Scheme 1.

In one of the large fractions the elemental composition was determined to be 87.0% C, 8.7% H and 4.2% N. The proton distribution in the NMR spectra of NNC I–NNC III is given in Table II.

The retention times of the reference compounds under the same conditions as for the GC analysis are as follows: carbazole, 19.8; N-methylcarbazole, 14.8; 1,4-dimethylcarbazole, 27.1; 1,4,6,8-tetramethylcarbazole, 32.5; 3,4-benzocarbazole, 49.9 min.

The GC separations of the fractions isolated are shown in Figs. 1–3. The identification data for the homologous series of carbazole derivatives and benzo analogues are summarized in Tables III–V, while Fig. 4 presents their quantities in a three-dimensional histogram. The distribution of NNCs of the carbazole type is given in Table VI.

DISCUSSION

A high content of carbazole and its alkyl derivatives was established in all the samples tested. The observations of Boduszynsky *et al.*[22], Shiller[23] and Bodzek *et al.*[24]

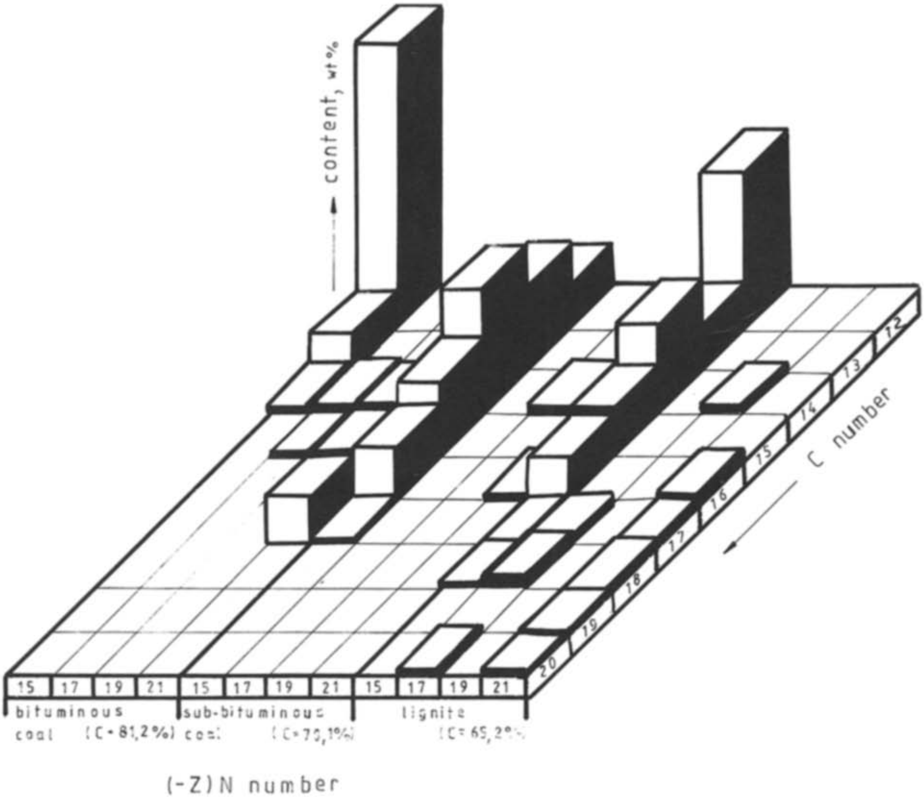


Fig. 4. Distribution of carbazole-type NNCs in coal liquefaction asphaltenes.

TABLE III

NEUTRAL NITROGEN COMPOUNDS OF THE CARBAZOLE TYPE IDENTIFIED IN SAMPLE NNC I

No. of peak	*Z*	*MW*	*Retention time (min)*	*Structure proposed*	*Content (rel. %)*		*Identification methods*
					Of the peak	*Total of the homologue*	
1	−15	167	20.2	Carbazole	35.2	36.7	GC, GC–MS
2	−15	167	20.8	Benzoindole	1.5		GC–MS
3	−15	181	23.5	1-Methylcarbazole	3.3	10.3	GC–MS
4	−15	181	24.1	3-Methylcarbazole	1.8		GC–MS
5	−15	181	24.3	2-Methylcarbazole	2.7		GC–MS
6	−15	181	25.7	4-Methylcarbazole	2.5		GC–MS
7	−15	195	26.4	C_2-alkylcarbazole	0.6	18.0	GC–MS
8	−15	195	27.3	1,4-Dimethylcarbazole	1.8		GC, GC–MS
9	−15	195	27.5	C_2-alkylcarbazole	1.7		GC–MS
10	−15	195	27.6	C_2-alkylcarbazole	2.4		GC–MS
11	−15	195	28.0	C_2-alkylcarbazole	1.0		GC–MS
12	−15	195	28.1	C_2-alkylcarbazole	1.0		GC–MS
13	−15	195	28.2	C_2-alkylcarbazole	2.4		GC–MS
14	−15	195	29.0	C_2-alkylcarbazole	1.7		GC–MS
15	−15	195	29.6	C_2-alkylcarbazole	3.0		GC–MS
16	−15	195	30.0	C_2-alkylcarbazole	2.4		GC–MS
17	−15	209	30.5	C_3-alkylcarbazole	0.7	11.0	GC–MS
18	−15	209	30.9	C_3-alkylcarbazole	0.8		GC–MS
19	−15	209	31.3	C_3-alkylcarbazole	1.1		GC–MS
20	−15	209	31.5	C_3-alkylcarbazole	2.6		GC–MS
21	−15	209	31.8	C_3-alkylcarbazole	3.5		GC–MS
22	−15	209	32.2	C_3-alkylcarbazole	2.3		GC–MS
23	−15	223	33.1	C_4-alkylcarbazole	1.1	9.7	GC–MS
24	−15	223	33.4	1,4,6,8-Tetramethylcarbazole	1.6		GC, GC–MS
25	−15	223	33.6	C_4-alkylcarbazole	2.4		GC–MS
26	−15	223	33.9	C_4-alkylcarbazole	0.6		GC–MS
27	−15	223	35.0	C_4-alkylcarbazole	1.4		GC–MS
28	−15	223	35.4	C_4-alkylcarbazole	1.1		GC–MS
29	−15	223	35.6	C_4-alkylcarbazole	1.5		GC–MS
30	−15	237	37.5	C_5-alkylcarbazole	0.5	0.5	GC–MS
31	−15	251	41.3	C_6-alkylcarbazole	0.5	0.5	GC–MS
32	−19	191	43.4	Phenanthroindole	1.7	1.7	GC–MS
33	−21	217	48.1	Benzo[*a*]carbazole	3.6	5.0	GC–MS
34	−17	235	48.9	C_2-benzonaphthoindole	1.4	4.8	GC–MS
35	−17	249	49.6	C_3-benzonaphthoindole	2.7		GC–MS
36	−21	217	50.0	Benzo[*c*]carbazole	0.5		GC, GC–MS
37	−17	277	51.9	C_3-benzonaphthoindole	0.7		GC–MS
38–43	−21	231	54.4	C_1-benzocarbazole	0.3		GC–MS
45–47	−21	245	57.0	C_2-benzocarbazole	0.3		GC–MS
48, 49	−21	259	58.0	C_3-benzocarbazole	0.2		GC–MS
50	−21	273	60.0	C_4-benzocarbazole	0.1		GC–MS

that NNCs in asphaltenes in coal-derived liquids are of the carbazole type are thus corroborated.

As regards the substitution position from the ^{1}H NMR spectra, it can be concluded that this is of the C-alkyl type. No signal at 3.4–3.7 ppm, characteristic of an

TABLE IV

NEUTRAL NITROGEN COMPOUNDS OF THE CARBAZOLE TYPE IDENTIFIED IN SAMPLE NNC II

No. of peak	*Z*	*MW*	*Retention time (min)*	*Structure proposed*	*Content (rel. %)*		*Identification methods*
					Of the peak	*Total of the homologue*	
1	−15	167	19.2	Benzoindole	4.0	9.3	GC–MS
2	−15	167	20.0	Carbazole	5.3		GC, GC–MS
3	−15	181	22.5	1-Methylcarbazole	6.5	16.9	GC–MS
4	−15	181	23.1	3-Methylcarbazole	3.6		GC–MS
5	−15	181	23.2	2-Methylcarbazole	4.2		GC–MS
6	−15	181	24.0	4-Methylcarbazole	2.6		GC–MS
7	−15	195	26.3	C_2-alkylcarbazole	1.4	28.0	GC–MS
8	−15	195	26.5	C_2-alkylcarbazole	3.5		GC–MS
9	−15	195	26.6	C_2-alkylcarbazole	4.1		GC–MS
10	−15	195	27.0	C_2-alkylcarbazole	1.9		GC–MS
11	−15	195	27.1	1,4-Dimethylcarbazole	2.0		GC, GC–MS
12	−15	195	27.3	C_2-alkylcarbazole	4.9		GC–MS
13	−15	195	27.5	C_2-alkylcarbazole	1.0		GC–MS
14	−15	195	27.7	C_2-alkylcarbazole	1.3		GC–MS
15	−15	195	27.9	C_2-alkylcarbazole	1.5		GC–MS
16	−15	195	28.1	C_2-alkylcarbazole	1.6		GC–MS
17	−15	195	28.4	C_2-alkylcarbazole	1.3		GC–MS
18	−15	195	29.0	C_2-alkylcarbazole	2.5		GC–MS
19	−15	195	29.4	C_2-alkylcarbazole	1.0		GC–MS
20	−15	209	29.9	C_3-alkylcarbazole	2.1	15.9	GC–MS
21	−15	209	30.2	C_3-alkylcarbazole	3.0		GC–MS
22	−15	209	30.4	C_3-alkylcarbazole	4.1		GC–MS
23	−15	209	30.7	C_3-alkylcarbazole	3.2		GC–MS
24	−15	209	31.2	C_3-alkylcarbazole	3.5		GC–MS
25	−15	223	32.1	C_4-alkylcarbazole	1.1	12.3	GC–MS
26	−15	223	32.4	1,4,6,8-Tetramethylcarbazole	2.1		GC, GC–MS
27	−15	223	32.5	C_4-alkylcarbazole	2.1		GC–MS
28	−15	223	32.8	C_4-alkylcarbazole	0.6		GC–MS
29	−15	223	33.0	C_4-alkylcarbazole	1.8		GC–MS
30	−15	223	33.9	C_4-alkylcarbazole	1.7		GC–MS
31	−15	223	34.3	C_4-alkylcarbazole	0.9		GC–MS
32	−15	223	34.6	C_4-alkylcarbazole	0.6		GC–MS
33	−15	223	35.5	C_4-alkylcarbazole	1.4		GC–MS
34	−15	237	36.5	C_5-alkylcarbazole	0.6	0.6	GC–MS
35	−19	191	42.3	Phenanthroindole	1.7	1.7	GC–MS
36	−21	217	47.1	Benzo[*a*]carbazole	1.7	2.5	GC–MS
37	−21	217	49.6	Benzo[*c*]carbazole	0.8		GC, GC–MS

N-alkyl bond, was observed. Also the signal for the N–H non-substituted proton at 7.3–7.5 ppm is clearly expressed. The GC study of the samples and that of the reference N-methylcarbazole revealed the lack of this compound in the mixture under investigation.

The ^{1}H NMR spectra of samples NNC I and NNC II are rather similar, as seen from Table II. They are characterized by an high content of H_α proton, indicating a high degree of substitution. This finding was confirmed by the GC–MS analysis. In

TABLE V

NEUTRAL NITROGEN COMPOUNDS OF THE CARBAZOLE TYPE IDENTIFIED IN SAMPLE NNC III

No. of peak	*Z*	*MW*	*Retention time (min)*	*Structure proposed*	*Content (rel. %)*		*Identification methods*
					Of the peak	*Total of the homologue*	
1	−15	167	19.8	Carbazole	63.7	65.8	GC, GC–MS
2	−15	167	20.5	Benzoindole	2.1		GC–MS
3	−15	181	22.4	1-Methylcarbazole	3.9	7.9	GC–MS
4	−15	181	23.2	3-Methylcarbazole	1.1		GC–MS
5	−15	181	24.0	2-Methylcarbazole	2.3		GC–MS
6	−15	181	24.7	4-Methylcarbazole	0.6		GC–MS
7	−19	191	43.1	Phenanthroindole	1.6	1.6	GC–MS
8	−21	217	47.7	Benzo[*a*]carbazole	11.0	18.5	GC–MS
9	−21	217	49.6	Benzo[*c*]carbazole	7.5		GC, GC–MS

sample NNC III the content of H_α proton decreases steeply, while that of the naphthenic protons (H_β) increases. Most probably, part of sample is non-volatile under the analysis conditions and the NNCs are of the naphthoindole and naphthocarbazole types. No compounds of the series $Z(N) = -23$ were determined in the samples studied, *e.g.*, phenylcarbazoles, which are characteristic for the high-boiling petroleum fractions and residues, are not present.

The carbazole content is very high as revealed by calculation of the GC separations. In the MS analysis it was found that, besides the peak of carbazole with the same retention time as that of the reference, there are also peaks with relatively low contents and the same molecular masses, M^+ at m/z 167. Similar observations were reported by Later *et al.*[25] for the analysis of CDLs. Their spectral data indicate the presence of carbazole structural isomers, which were identified as 1*H*-benz[*g*]indole and 3*H*-benz[*e*]indole. In a similar way we could explain the presence of the components in our mixture.

The content of C_1-carbazole, M^+ at m/z 181, is high. All of the possible four

TABLE VI

DISTRIBUTION OF NEUTRAL NITROGEN COMPOUNDS OF THE CARBAZOLE TYPE IN THE DIFFERENT Z(N) SERIES

Z(N)	*Content (rel. %)**		
	NNC I	*NNC II*	*NNC III*
−15	86.7	83.0	73.7
−17	4.8	–	–
−19	1.7	1.7	1.6
−21	5.0	2.5	18.5

* All calculations are for the volatile part of the sample.

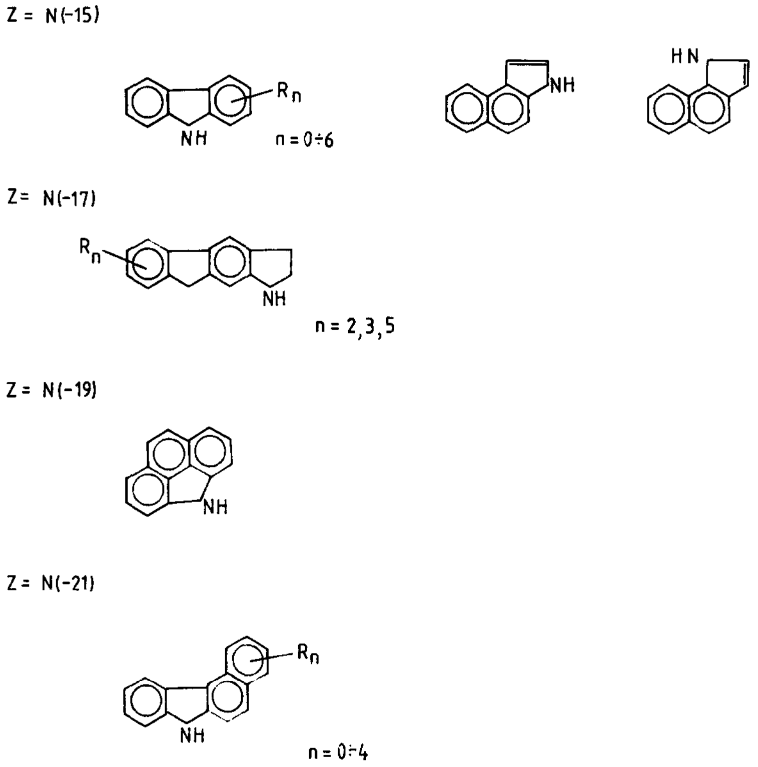


Fig. 5. Structures proposed.

positional isomers have been checked. According to the empirical rules deduced by Dorbon *et al.*[15] concerning the elution order of methylcarbazoles, a relationship was written as follows $1 < 3 < 2 < 4$ (where the number denotes the position of the substituent) which was valid for asymmetric C_2-carbazoles with only a few exceptions. The elution order for C_3-alkylcarbazoles (trimethylcarbazoles) followed the same trends, as observed by Ignatiadis *et al.*[17,19]. From the elution order of methylcarbazoles the positions of the substituents were proposed. Thirteen out of the possible sixteen C_2-alkylcarbazoles positional isomers have been checked. The exact position of 1,4-dimethylcarbazole was determined by use of a standard. For th C_3-alkylcarbazoles, we detected 6 out of the 28 possible isomers, while for the C_4-alkylcarbazoles we found 7 out of over 58 combinations. The uncertainity in identification increases when not only methyl but also ethyl derivatives are possible. The presence of a base ion at $m/z = M^+ - 29$ corresponding to the ethyl scission is an indication of an ethyl substitution. Such fragments were detected in the mass spectra of C_5-, C_6-alkylcarbazoles. Bearing in mind the low content of homologues, we assumed that the amount of ethyl derivatives was negligible. The ^{1}H NMR spectra of samples NNC I and NNC II provide support for this assumption, since signals of the CH_2 groups at α position with respect to the aromatic ring are recorded. A longer chain is unlikely. In neither of the mass spectra is there a base ion with a mass $m/z = 180$, corresponding to the β-splitting of the chain and the formation of the tropylium ion from the carbazole aromatics.

The series next most abundant is that with $Z(N) = -21$. Benzo[*a*]- and benzo[*c*]carbazole have been observed, while benzo[*b*]carbazole has not been detected, while observed in small amount by Dorbon *et al.*[16] and Ignatiadis *et al.*[14]. Alkyl derivatives, C_1–C_4 radicals, were also observed. The series $Z(N) = -19$ is present in small amount with only one representative, M^+ at m/z 191, found in all three samples studied. This compound was reported also by Borra *et al.*[12]. These authors assign it as a first member of the homologous series of nitrogen-containing molecules of the pyrrole type with 8–10 fused aromatic rings.

The series $Z(N) = -17$, with M^+ at m/z 235, 249, 277 have been detected in one of the samples, NNC I. With respect to its retention time, it is partially overlapped by the series $Z(N) = -21$ and perhaps this explains the fact that the compound with 19 carbon atoms was not detected. This series is of the naphthocarbazole type and illustrates one of the possible ways for the formation of the higher-boiling compounds, non-volatile under these analysis conditions. This series was found by Kiselev *et al.*[13] in high-boiling fractions of West Siberian petroleum. The structures of the compounds detected are given in Fig. 5.

CONCLUSIONS

The chromatographic approach proposed for the analysis of coal asphaltenes is suitable for the isolation of carbazole-type nitrogen compounds. It is found that the content of carbazole and its alkylated derivatives is one order of magnitude larger than that of other homologous series. The substitution is of the C-alkyl type, whereby the number of the substituents reaches 4–6. The presence of ethyl radicals in the–A derivatives of carbazole is not excluded, but their relative amounts are negligible compared with the methyl substituents. The following homologous series were found in neutral nitrogen compounds of coal asphaltenes: $Z(N) = -15, C_{12}$–$C_{18}; -17, C_{17}, C_{18}, C_{20}; -19, C_{14}; -21, C_{16}$–$C_{20}$.

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