


Article

# <sup>1</sup>H-NMR Spectroscopy: A Possible Approach to Advanced Bitumen Characterization for Industrial and Paving Applications

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**Abstract:** Bitumen has unique chemo-mechanical properties, and for this reason, it is today one of the main constituents of many industrial products beside its common use in highway pavements construction. While the excellent rheological properties of bitumens have been investigated by means of different techniques, much remains to be known about the intrinsic properties of this complex material. It is therefore important to investigate its structure and properties from a closer point of view, towards possible useful modifications of the neat material. The present research developed a technique to investigate the composition of bitumens using Thin Layer Chromatography (TLC) to separate the different fractions, and Nuclear Magnetic Resonance (NMR) spectroscopy to assess and quantify the aliphatic hydrogen part with respect to the aromatic part. To achieve a comprehensive understanding of the chemical composition of the materials, Proton Nuclear Magnetic Resonance (<sup>1</sup>H-NMR) analysis was conducted in solution, using CCl<sub>4</sub> as solvent, on three different neat bitumens and on their asphaltene and maltene fractions. The combined application of TLC and <sup>1</sup>H-NMR spectroscopy enables the advanced characterization of bitumens supplied from different sources or obtained from different processes. This further allows addressing the use of specific modifications according to the bitumen final applications.

**Keywords:** bitumen; chemo-mechanical properties; Thin Layer Chromatography (TLC); Nuclear Magnetic Resonance (NMR) spectroscopy

## 1. Introduction

### 1.1. Background

Bitumen, as one of the materials obtained from crude oil, is a viscoelastic material, which is remarkably soluble in carbon disulfide (CS<sub>2</sub>) and holds adhesive and waterproofing properties. From the chemical point of view, bitumen contains approximately 80% carbon, 15% hydrogen and the remaining part consists of two types of atoms: heteroatoms and metals [1]. Considering the chemical composition, it is highly dependent on the source (crude oil) and on the refinery process, which contribute to its unique chemical and physical properties [2]. Although in this context chemistry of bitumen has been considered as a key parameter in fundamental understanding of bitumen characterization, the knowledge about such a complex material is still limited. Bitumen is typically constituted of two main groups of compounds: (a) asphaltenes, defined as *n*-heptane-insoluble and toluene-soluble part,

which are complex mixtures of high molecular weight hydrocarbons present in a percentage ranging between 5% and 25% by weight, consisting mainly of condensed aromatic compounds, as well as oxygen, nitrogen, sulfur and metals; and (b) maltenes, as soluble part in *n*-heptane, can in turn be subdivided into saturates, aromatics, and resins, which, together with the asphaltenes, are known as SARA fractions [3]. While asphaltenes have the highest polarity, saturates are the least polarized molecules following the aromatics and resins, which rank in between the two extremes. Several former studies have indicated that the relative amount of bitumen fractions considerably affect both the physical and mechanical properties. It has been found that, while the polar fraction directly affects the elastic phase, the presence of non-polar fraction contributes to the viscous behavior of bitumen [4]. Therefore, a better understanding of the structural characteristics and composition of the various fractions is of utmost importance in the industrial use of these complex mixtures to apply appropriate methodologies to adapt their chemical-physical properties in a controlled manner [5,6].

Since the bitumen fractions obviously determine the bitumen mechanical properties and characteristics, several attempts have been made to analyze the bitumen composition and to fractionate the bitumen compounds. Beside Atomic Force Microscopy (AFM) images and Fourier Transform-Infrared Spectroscopy (FT-IR) analysis, recently Nuclear Magnetic Resonance (NMR) spectroscopy has been found to be a practically efficient and reliable technique for complex material characterization such as bitumen [7,8]. It is worth underlining that the NMR has become one of the most powerful tools for probing in all states of matter. The technique in isotropic solution is commonly used for the characterization of synthetic or natural compounds, while structural and conformational information on even large-sized molecules can be obtained in anisotropic media through the anisotropic NMR observables, such as the residual dipolar couplings (RDCs) [9–12].

Nowadays, the NMR technique is also well known as an analytical technique for qualitative and quantitative study, at molecular level, of complex mixtures. Compared to the conventional analysis, NMR spectroscopy does not need the pre-treatment of samples that could considerably reduce the time consuming process of their preparation. In addition, since the amount of solvent that is used and the waste generation is minimum, the technique is considered environmentally friendly [13]. The superiority of this technique is the ability to simultaneously investigate several components of the mixture with a single  $^1\text{H}$ -NMR spectrum and to evaluate the relative amount of the aliphatic and aromatic hydrogens portion in the mixture [8,14,15].

On the other hand, the separation technique to prepare a sufficient sample for NMR analysis can be a challenge. Among the proposed conventional methods to separate the bitumen fractions, Thin Layer Chromatography (TLC) and Liquid Chromatography (LC), known as qualitative and quantitative techniques in many fields such as organic, inorganic analytic and physical chemistry are commonly used [16–19].

TLC, compared to LC, requires milligram size samples, less solvent, and no deasphaltenization before the analysis, which makes it a rapid and affordable separation technique for bitumen [20]. It is worth mentioning that, despite the successfully employed TLC method for bitumen fractionation, the key point to obtain well-defined and separated spots is to select a stationary phase and an appropriate solvent or even mixed compound [21].

## 1.2. Objectives

Since the properties of bitumen and its use largely depend on its chemical composition, it is clear that significant improvements would result from a better understanding of the material at its molecular level. Starting with the difficulties highlighted in the characterization of chemical composition of bitumen, this research aimed to suggest and develop a new methodology for characterizing this complex mixture of organic compounds by combining the separation of the individual fractions via TLC with the high resolution  $^1\text{H}$ -NMR technique. Note that TLC was selected considering all benefits of this technique compared to LC. Moreover, since conventional bitumens are primarily used in road

pavements and the modification of their mechanical properties is often required in any field, a deeper knowledge of bitumen composition would be of outermost importance.

Therefore, the main goal of this work was the characterization of three commercial bitumens, with different degrees of penetration (traditional penetration test), using the  $^1\text{H}$ -NMR spectra recorded on the neat bitumen and on their fractions obtained through silica preparative TLC.

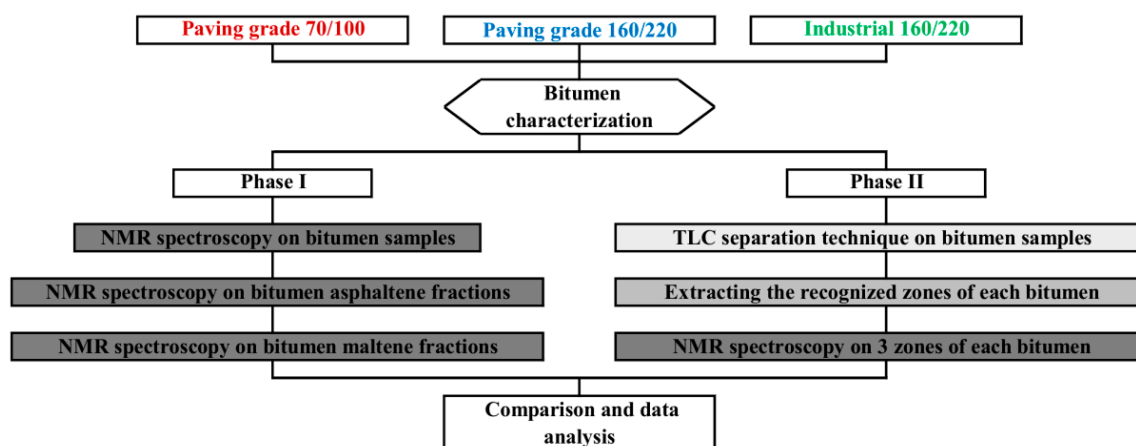
## 2. Materials and Methods

The bitumens used in this work are three commercial ones having penetrations ranging between 70 and 220 dmm (one penetration unit = 0.1 mm, Table 1). Penetration value test on bitumen is a measure of hardness or consistency of bituminous material. A 70/100 grade bitumen indicates that its penetration value lies between 70 and 100. Penetration value is the vertical distance traversed or penetrated by the point of a standard needle into the bituminous material under specific conditions of load, time and temperature. This distance is measured in one tenths of a millimeter. The two soft bitumens having the same class of penetration (160/220) have similar physical properties, while they have different origins and are processed by different techniques. They were selected to ascertain whether their chemical compositions are equal or different [22]. In the literature, it has been shown that, while two bitumens have the same softening point and penetration grade, they may show significant difference from the chemical point of view [22,23]. In addition, a 70/100 paving grade bitumen was also investigated to understand the effects of different bitumen processing on bitumen fundamental chemical properties.

**Table 1.** Fundamental physical properties of bitumens.

Measured Properties	Standard	Unit	Paving Grade	Paving Grade	Industrial
			70/100	160/220	160/220
Penetration at 25 °C	EN 1426	0.1 mm	70–100	160–220	170
Softening point (R&B)	EN 1427	°C	43–51	35–43	35–43
Flash point	EN 2592	°C	≥230	≥220	271
Solubility	EN 12592	% (m/m)	≥99	≥99	≥99
Mass change at 163 °C	EN 12607-1	%	≤0.8	≤1	≤1
Retained penetration	EN 1426	%	≥46	≥37	≥37
Increase in softening point	EN 1427	°C	≤9	≤11	≤12

The diagram shown in Figure 1 illustrates the main methodology followed in this research. In the first phase,  $^1\text{H}$ -NMR spectra were recorded on untreated bitumen samples and on asphaltene and maltene fractions separated from the three bitumens using *n*-pentane as a solvent, with a slightly modified method compared to the commonly used one. The separation procedure is explained later.



**Figure 1.** Research scheme.

In the second phase, the  $^1\text{H}$ -NMR spectroscopy was applied to the separated zones extracted from each bitumen by preparative TLC.

### 3. Experimental Work

#### 3.1. Bitumen Separation Techniques

In the present research, two different separation techniques have been used to separate test bitumens into fractions and prepare samples for the following analysis: the conventional method and Thin Layer Chromatography (TLC). It is worth mentioning that TLC was applied as qualitative and quantitative technique for bitumen fractions analyses using a ternary mixture of Methanol/Tetrahydrofuran/Chloroform (3:3:4 *v/v/v*) as solvent.

##### 3.1.1. Asphaltenes and Maltenes Separation (Modified Conventional Method)

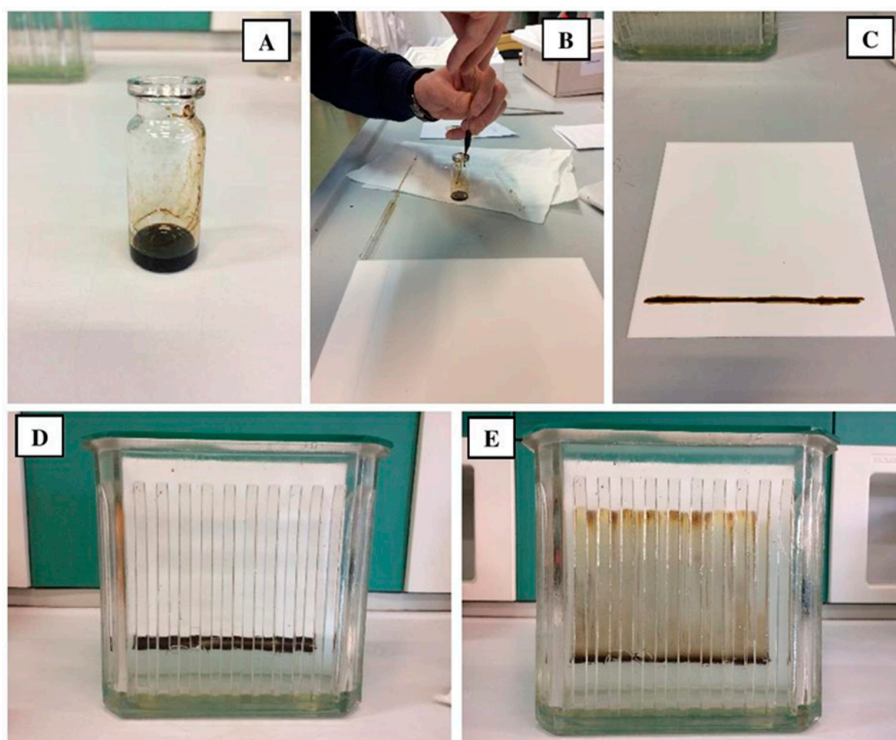
In a vessel, a volume in milliliters of  $\text{CHCl}_3$  was combined to a corresponding amount in grams of bitumen (e.g., 3 g of bitumen for 3 mL of  $\text{CHCl}_3$ ) and the mixture was carefully dissolved. Then, a volume of *n*-pentane forty times the  $\text{CHCl}_3$  volume was added to the solution, which was left in dark for two hours, mixing occasionally. Finally, the precipitated asphaltenes were filtered in a funnel with paper filter by vacuum (Whatman 42 ashless). The residue was washed several times with *n*-pentane until solvent became colorless. The filter paper was dried in oven at 80 °C for three hours and successively the residue of the solvent was removed in vacuum for two hours. The filtrate, containing maltene portion, was evaporated to dryness with a rotary evaporator under reduced pressure and the residual solvent removed under vacuum pump.

##### 3.1.2. Thin Layer Chromatography (TLC)

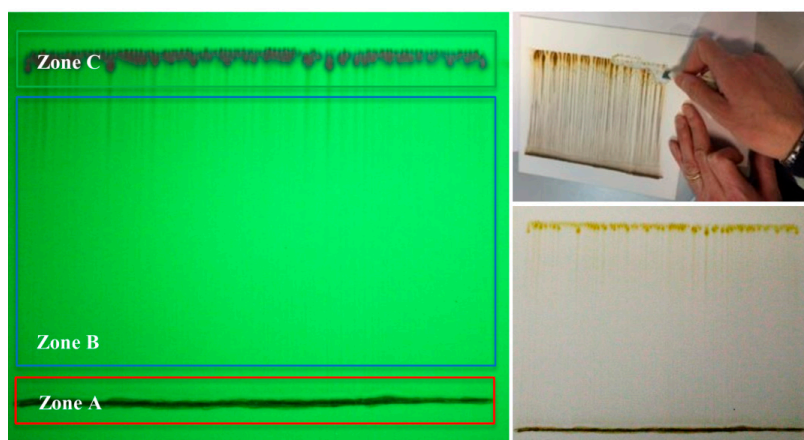
TLC separation technique was performed on Merck glass plates (silica gel coated with fluorescent indicator F254; gel thickness: 0.25 mm and 1 mm for qualitative and quantitative analysis, respectively), with MeOH/THF/ $\text{CHCl}_3$  mixture (3:3:4 *v/v/v*) as eluent [24]. Preliminary tests on neutral alumina plates and silica gel plates were performed to select the stationary phase. The results confirmed a higher separation of bitumen samples by silica gel as stationary phase. Noteworthy, given that the bitumen stiffness and mechanical properties are related to the asphaltene content, the method has been applied for both bitumens with asphaltene and deasphaltized bitumens. Dichloromethane (DCM) was used to solubilize the sample by mixing 0.04–0.05 g of bitumen to the amount of DCM needed to provide a homogenous solution (Figure 2A). The performed procedure is illustrated in Figure 2 and consists of some steps. Firstly, all prepared samples were spotted on the silica gel plate with a pipette as spotter (Figure 2B,C). Subsequently, the plate was placed in a glass eluent container (separation chamber) until the solvent rises through 90% of the plate (Figure 2D,E). Finally, the plate was removed from separation chamber and exposed to the UV lamp, Shortwave 254 nm (Figure 3). The visualization under ultraviolet (UV) light is surely the most used revelation technique to check molecules with chromophore groups and, for this reason, we chose to use it to observe the separated spots.

Figure 3 shows three main zones (A, B and C) visualized under UV lamp that were separated by scraping off the silica with a scraper and transferring it to three flasks respectively. Methanol (100 mL) was added to each flask, the flasks were swirled for 30 min, and the contents were allowed to sediment. The supernatant solution was pipetted off and centrifuged. This procedure was repeated three times for each sample using same volume of methanol, and the combined extracts were evaporated to dryness in vacuo. Using this procedure, we obtained the three separated fractions as thick mass.

Considering the complex composition of bitumen, in this first phase, we only hypothesized that Zone A (red frame) should match with the asphaltene fraction of bitumen, considering the absence of this spot in preliminary TLC tests on bitumen samples without asphaltene. Subsequently, all separated fractions have been analyzed by  $^1\text{H}$ -NMR technique.



**Figure 2.** TLC technique procedure in chronology (A–E).



**Figure 3.** Separated spots on silica gel plate (160/220 Industrial bitumen sample). Three distinguished zones visualized under UV irradiation at 254 nm on the left and the scratching the zones on the top of right.

### 3.2. Nuclear Magnetic Resonance Spectroscopy (NMR)

The  $^1\text{H}$ -NMR spectra were recorded at room temperature on a high-resolution Bruker Avance 500 MHz spectrometer (11.74 T) (Bruker, Rheinstetten, Germany) equipped with a 5 mm TBO probe (Triple Resonance Broadband Observe) and a standard variable-temperature unit BVT-3000. Each sample was prepared using  $\text{CCl}_4$  as a solvent to prevent any overlapping of protonic signal due to the solvent. The  $^1\text{H}$ -NMR experiments were performed using 20 mg of bitumen diluted in 0.5 mL of  $\text{CCl}_4$ . Typical  $^1\text{H}$ -NMR signal positions are reported in Table 2 commonly used for NMR data interpretation. If the protons associated to the heteroatoms are neglected, the NMR spectrum is characterized by five types of proton groups: aromatic protons ( $H_{\text{ar}}$ ; 6–9 ppm), olefinic protons ( $H_{\text{ol}}$ ;



4–6 ppm), alpha-alkyl protons ( $H_\alpha$ ; 2–4 ppm), alkyl protons, primarily the methylene protons which are  $\beta$  or farther from the aromatic ring ( $H_\beta$ ; 1–2 ppm) and the methyl protons in the  $\gamma$  position or farther from the aromatic ring ( $H_\gamma$ ; 0.5–1 ppm). The fractions of asphaltenes, maltene and products obtained from TLC were used to prepare the NMR samples, using for each sample  $\approx 20$  mg of substance and 0.5 mL of  $\text{CCl}_4$  as solvent.

**Table 2.** Types of protons and chemical shift assignments [25].

Parameter	Chemical Shift	Type of Protons
$H_{\text{ar}}$	6.0–9.0	Aromatic hydrogen
$H_{\text{ol}}$	4.0–6.0	Olefinic hydrogen
$H_\alpha$	2.0–4.0	Aliphatic Hydrogen on $\text{C}_\alpha$ to aromatic rings
$H_\beta$	1.0–2.0	Aliphatic Hydrogen on $\text{C}_\beta$ and the $\text{CH}_2$ beyond the $\text{C}_\beta$ to aromatic rings
$H_\gamma$	0.5–1.0	Aliphatic Hydrogen on $\text{C}_\gamma$ and the $\text{CH}_3$ beyond the $\text{C}_\gamma$ to aromatic rings

#### 4. Results and Discussion

Due to the complex nature of bitumen and difficulties in distinguishing the discernible differences in the bitumens with similar physical properties, a comprehensive analysis requires detailed integration of chromatographic and spectroscopic data. In the context, it was shown that, for discriminating the differences of various bitumens, the understanding of structural and functional entities in asphaltene is playing a key role. It was found that asphaltene from different bitumens have different structural characteristics [22]. For this reason, in the present research, the  $^1\text{H}$ -NMR analysis was conducted on both asphaltene and maltene fractions along with the bitumen samples. The  $^1\text{H}$ -NMR spectra of the analyzed bitumens including neat samples, asphaltene, and maltene fractions are shown in Figures 4–6. All three spectra show a very similar distribution of signals: two strong absorption peaks at 0.85 and 1.25 ppm, which correspond to proton on methyl and methylene groups, respectively; and some other large bands at 2.3–3.8 ppm and at 5.8–8.5 ppm that correspond to alkyl proton on  $\text{C}_\alpha$  and to aromatic protons, respectively. It should be noted that, in all spectra, no signal in the 4.5–6 ppm region is recorded, typically the olefinic region, which means that the amount of olefinic hydrocarbons, although present, is negligible. The four regions selected for each spectrum were integrated and normalized to get the fractional proton distributions directly from the integration curve. The fractional proton distributions of the three bitumen samples are given in Table 3.

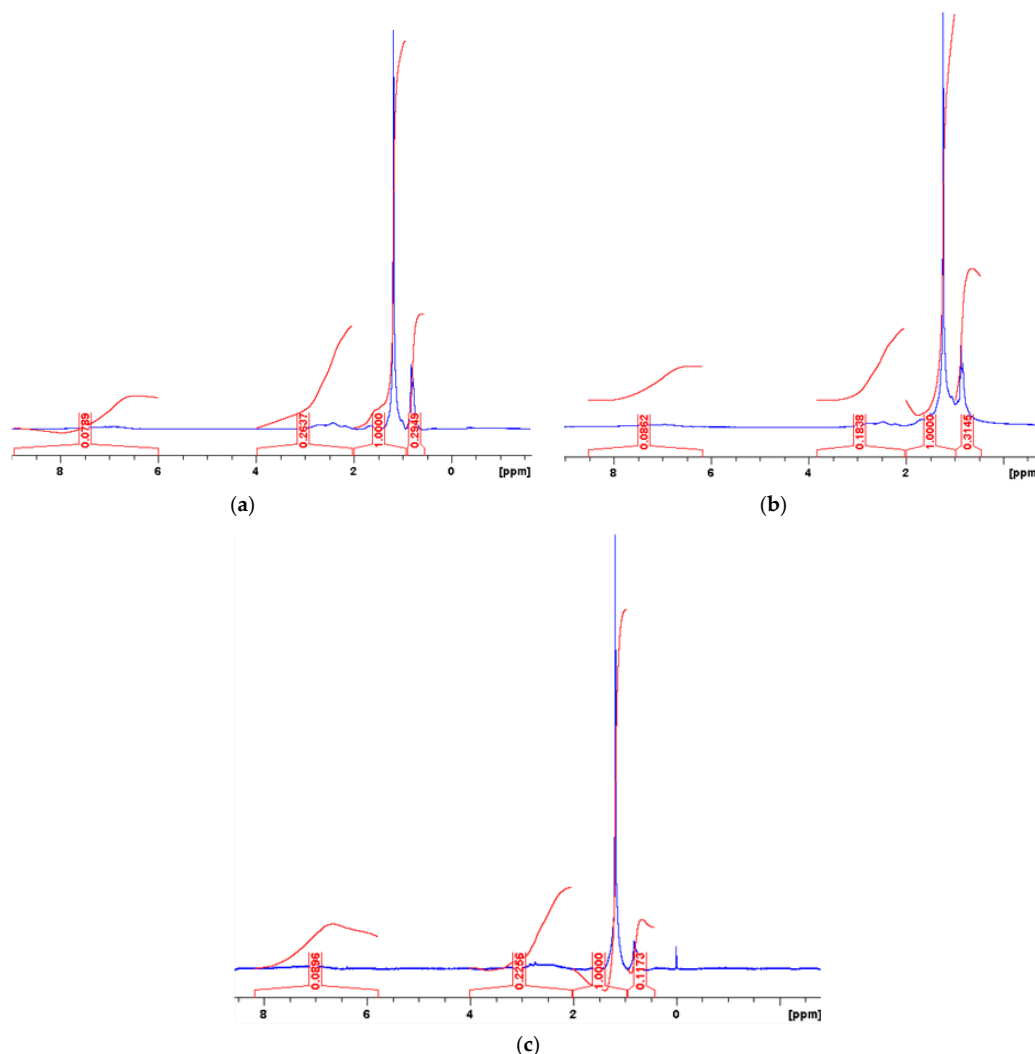
**Table 3.** Fractional proton distribution of the three bitumens obtained from the  $^1\text{H}$ -NMR spectra reported in Figures 4, 5 and 6a.

Bitumen	Hydrogen Distribution $\pm 0.05$			
	$H_{\text{ar}}$	$H_\alpha$	$H_\beta$	$H_\gamma$
Paving 70/100	8.00	3.86	64.38	23.73
Paving 160/220	8.32	3.80	64.19	23.66
Industrial 160/220	4.82	16.10	61.07	18.00

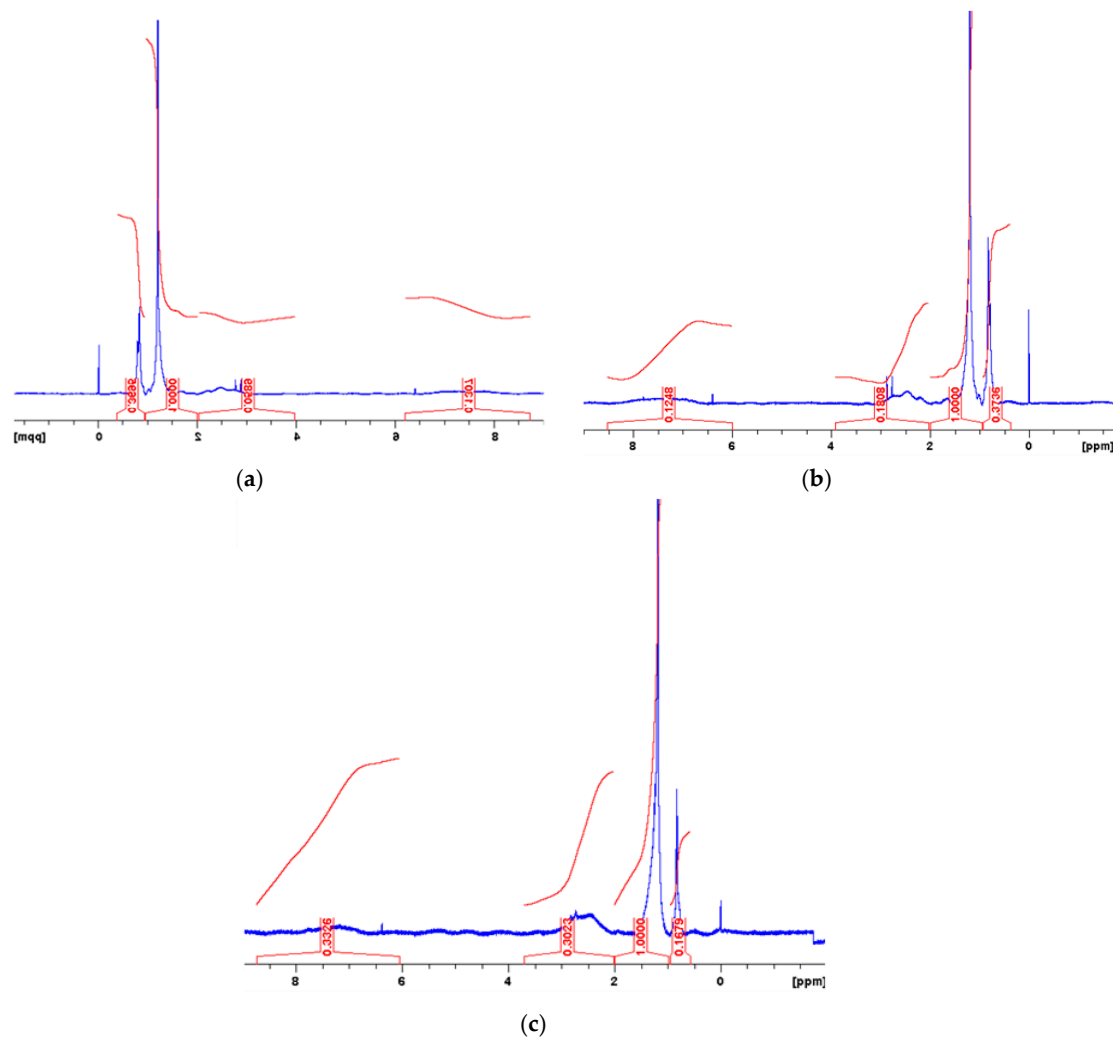
Comparing the values of hydrogen distribution reported in Table 3, it can be observed that the two paving bitumens have a similar distribution of hydrogen types, while the distribution corresponding to the industrial bitumen is very different from the first two. In detail, the area corresponding to the aromatic zone is nearly the same in the first two samples (8.00% and 8.32%), while it is markedly lower in the last one (4.82%). On the contrary, the industrial bitumen is characterized by a high percentage of aliphatic protons compared to the other bitumens (95.17% vs.  $\approx 91.90\%$ ), most of them corresponding to aliphatic hydrogens in  $\alpha$  relative to aromatic rings, since, as can be seen in Table 3, the hydrogen percentage  $H_\alpha$ , relating to the sample of industrial bitumen is much larger than the other two samples (16.10% vs.  $\approx 3.8\%$ ). This means that the nature of the compounds of the first two samples is similar,

and rather different from the third sample. It should be here reminded that, while the second paving grade bitumen and the industrial bitumen have the same classification grade, they originated from two different processes, which affect their final chemical compositions.

In the next stage, for each bitumen, the fractions of maltene and asphaltene extracted using the mentioned procedure were analyzed. Thereafter, each fraction was dissolved in  $\text{CCl}_4$  and the  $^1\text{H}$ -NMR spectrum was recorded for the provided samples. The  $^1\text{H}$ -NMR spectra of Maltene and Asphaltene fractions are reported respectively in Figures 4b, 5b and 6b and in Figures 4c, 5c and 6c, while, in Table 4, fractional proton distributions of each samples are reported. Observing the results of  $^1\text{H}$ -NMR analysis (Table 4), it is evident, as expected, that a higher percentage of aromatic hydrogen is present in the asphaltene fractions for all samples. Comparing the results for the asphaltene fractions, extracted from the three bitumens, it can be noted that the samples from the two bitumens with the same grade present a similar distribution of aromatic and aliphatic hydrogens ( $\approx 19\%$  and  $\approx 81\%$ , respectively), while the distribution of aliphatic hydrogen type is rather different. On the contrary, asphaltenes extracted from the paving bitumen (70/100) were characterized by a lower percentage of aromatic hydrogens. These data seem to point to a similar chemical composition for the asphaltene samples obtained from the two bitumen with the same degree of penetration and a different chemical composition for the asphaltene deriving from the paving bitumen (70/100).



**Figure 4.** The  $^1\text{H}$ -NMR spectra of Paving 70/100 bitumen in  $\text{CCl}_4$ : (a) neat bitumen; (b) maltene fraction; and (c) asphaltene fraction.



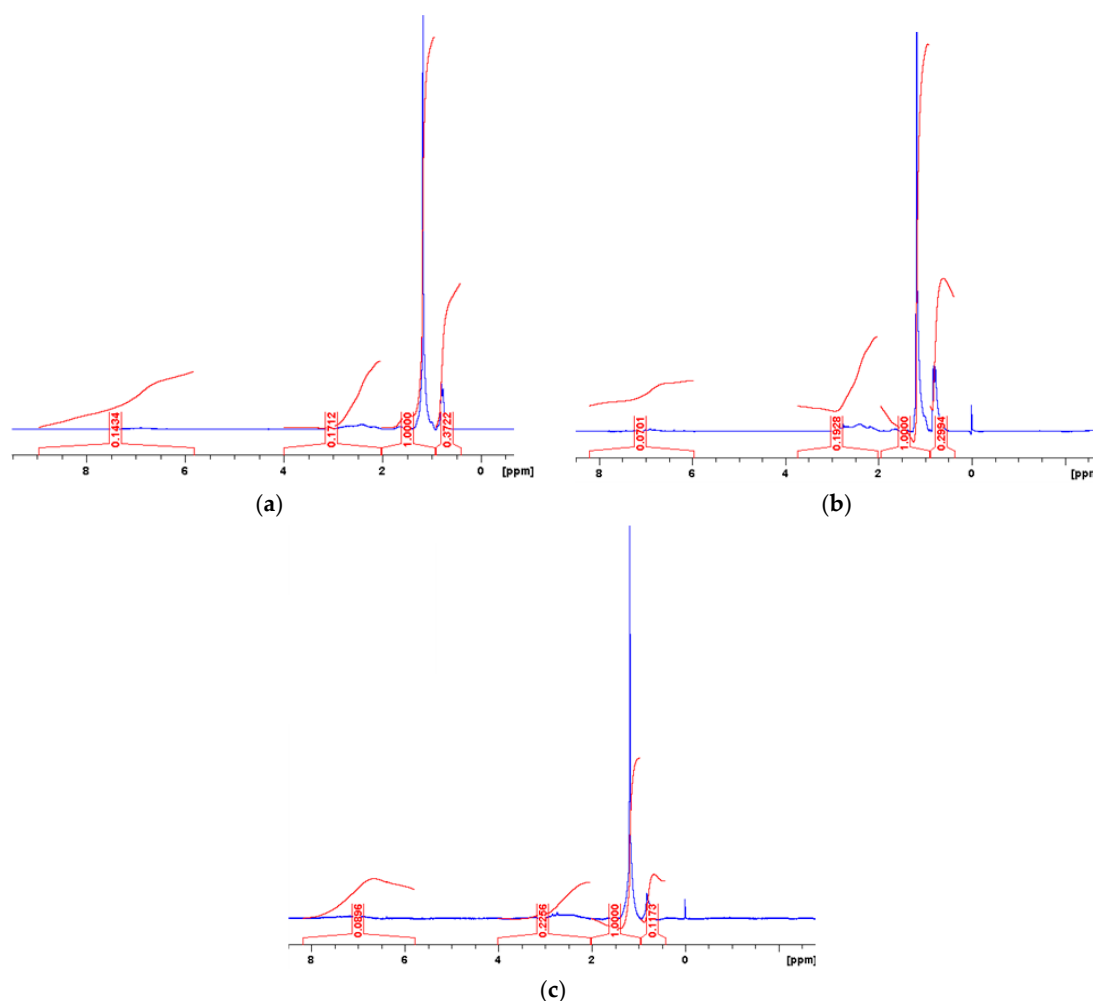
**Figure 5.** The  $^1\text{H}$ -NMR spectra of Paving 160/220 bitumen in  $\text{CCl}_4$ : (a) neat bitumen; (b) maltene fraction; and (c) asphaltene fraction.

**Table 4.** Fractional proton distribution of the maltene and asphaltene fractions obtained from the  $^1\text{H}$ -NMR spectra reported in Figure 4b,c, Figure 5b,c and Figure 6b,c.

Bitumen	Hydrogen Distribution of Maltenes $\pm 0.05$				Hydrogen Distribution of Asphaltenes $\pm 0.05$			
	$H_{\text{ar}}$	$H_{\alpha}$	$H_{\beta}$	$H_{\gamma}$	$H_{\text{ar}}$	$H_{\alpha}$	$H_{\beta}$	$H_{\gamma}$
Paving 70/100	4.49	12.34	64.01	19.16	14.25	15.75	61.80	8.19
Paving 160/220	7.43	11.77	60.55	20.24	18.30	16.77	55.47	9.31
Industrial 160/220	7.54	11.61	61.00	19.86	19.58	8.19	60.79	11.44

Moreover, the NMR data on the maltene fraction extracted from the two bitumens with high penetration show almost equal distribution of aromatic and aliphatic hydrogens, while the maltene sample from the paving bitumen 70/100 presents a lower aromatic percentage if compared to the other samples (4.49% vs.  $\approx 7\%$ ). The results obtained on maltene and asphaltene fractions provided a better understanding of bitumens detailed characteristics needed for developing methods to improve their properties. For example, adding suitable substances, it will be possible to increase or decrease the aromatic percentage that could be the key to modulate the viscosity of bitumen. Considering the bitumen complex system, the resins (intermediate polarity compounds) play a crucial role in the mechanical properties and in general on the bitumen performance properties [26].





**Figure 6.** The  $^1\text{H}$ -NMR spectra of Industrial 2 160/220 bitumen in  $\text{CCl}_4$ : (a) neat bitumen; (b) maltene fraction; and (c) asphaltene fraction.

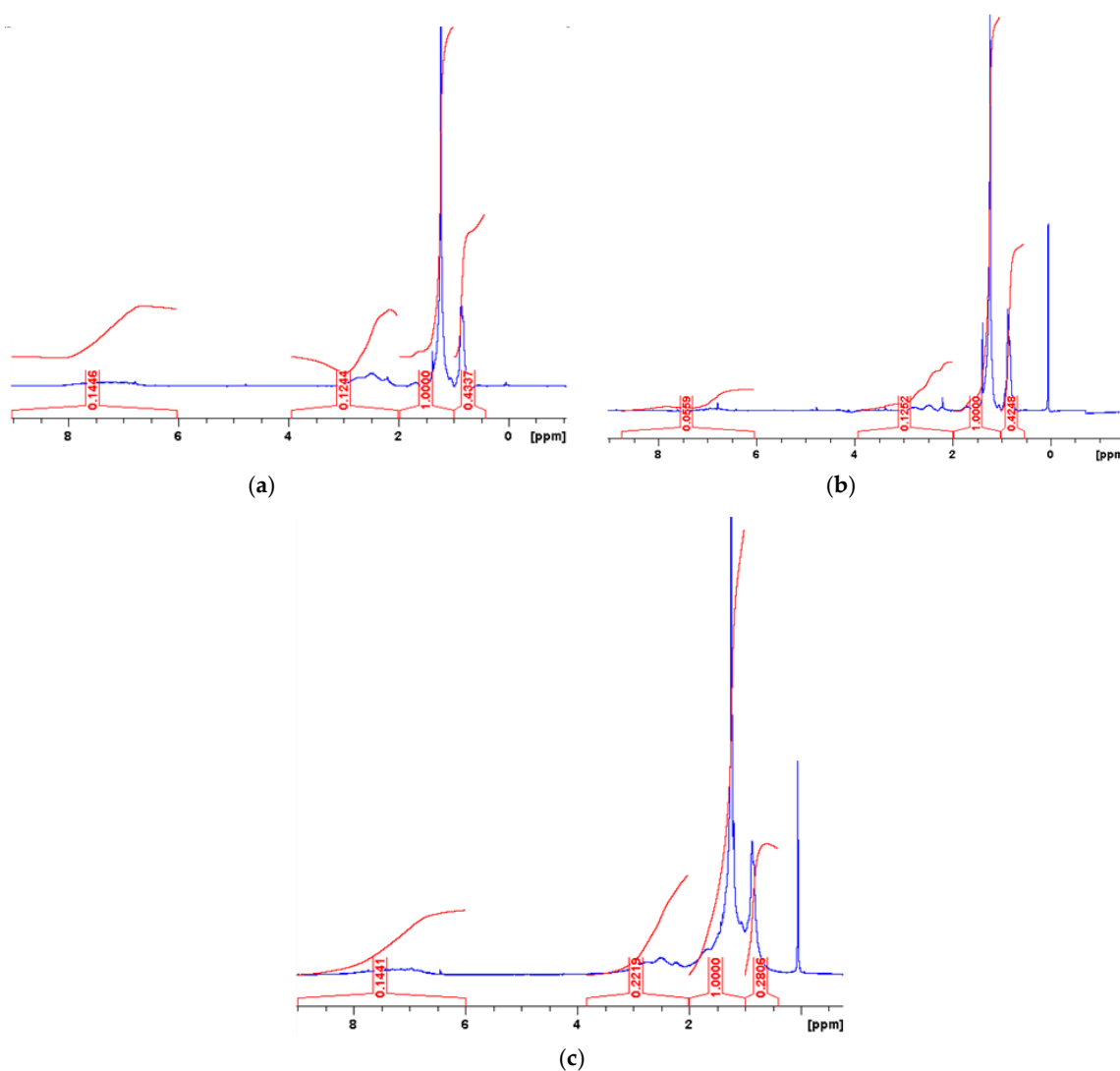
As mentioned earlier, for understanding the needed additives/modifiers to alter the characteristics of bitumens for specific uses, it is required to fractionate the bitumen with a preparative TLC and to analyze the obtained zones by NMR. The recognized three zones included: the C zone (on the top) should contain the apolar parts, i.e., the maltenes; the B zone is where the molecules with medium polarity are present; and the A zone, the lower spot, includes highly polar molecules. The B zone and A zone together should count for all the asphaltenes present in the sample. Table 5 lists the fractional proton distribution of the three zones obtained from the spectra reported in Figures 7–9. As it can be seen, data on hydrogens distribution confirm the hypothesis: the distribution related to zone C is similar in all samples to that found for maltenes extracted according to the classical procedure results (see Table 4). The hydrogens distribution of zone B is of particular interest: paving grade 70/100 and 160/220 bitumen samples are both characterized by a high percentage of aromatic hydrogen (22.47% and 32.19%, respectively) and by the presence of olefinic peaks in the aliphatic region. Moreover, the broad band of aromatic hydrogen was replaced by a fine structure of well-defined aromatic zones and with not much overlapping peaks. This probably means that, for these two bitumens, zone B is characterized by the presence of simple polyaromatic compounds that originate a fine structure. Instead, the sample of Industrial bitumen presents only aliphatic hydrogen, which corresponds to proton on methyl and methylene groups and no appreciable line/band at the aromatic zone.

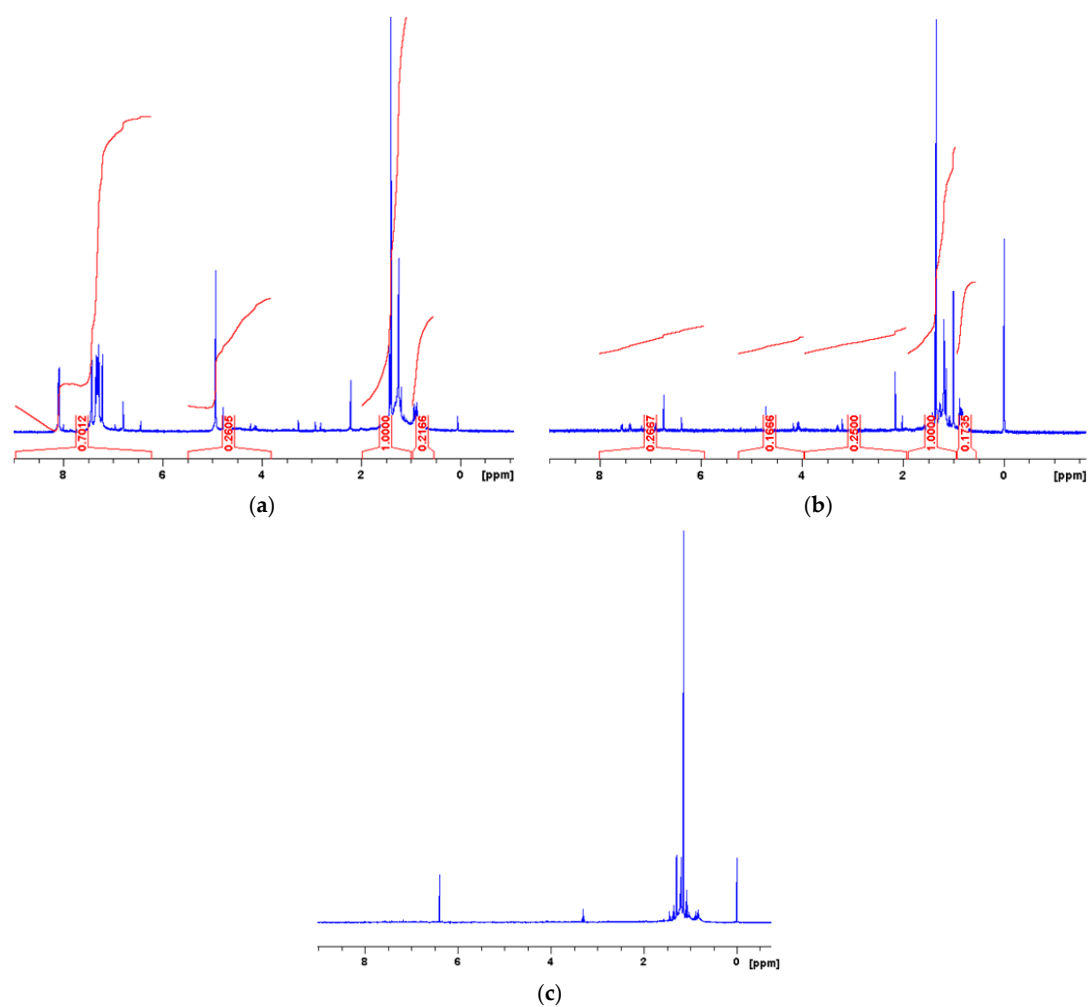
**Table 5.** Fractional proton distribution of various zones scratched from the three bitumens by preparative TLC obtained from the  $^1\text{H}$ -NMR spectra reported in Figures 7–9.

Bitumen	Hydrogen Distribution of Zone C $\pm 0.05$				Hydrogen Distribution of Zone B $\pm 0.05$			
	$H_{\text{ar}}$	$H_{\alpha}$	$H_{\beta}$	$H_{\gamma}$	$H_{\text{ar}}$	$H_{\text{ol}}/H_{\alpha}$	$H_{\beta}$	$H_{\gamma}$
Paving70/100	3.48	7.80	62.27	26.45	22.47	8.97/13.46	53.86	9.34
Paving 160/220	8.49	7.30	58.73	25.47	32.19	11.95 $H_{\text{ol}}$	45.91	9.94
Industrial 160/220	8.75	13.48	60.73	17.04	-	-	92.62	7.38

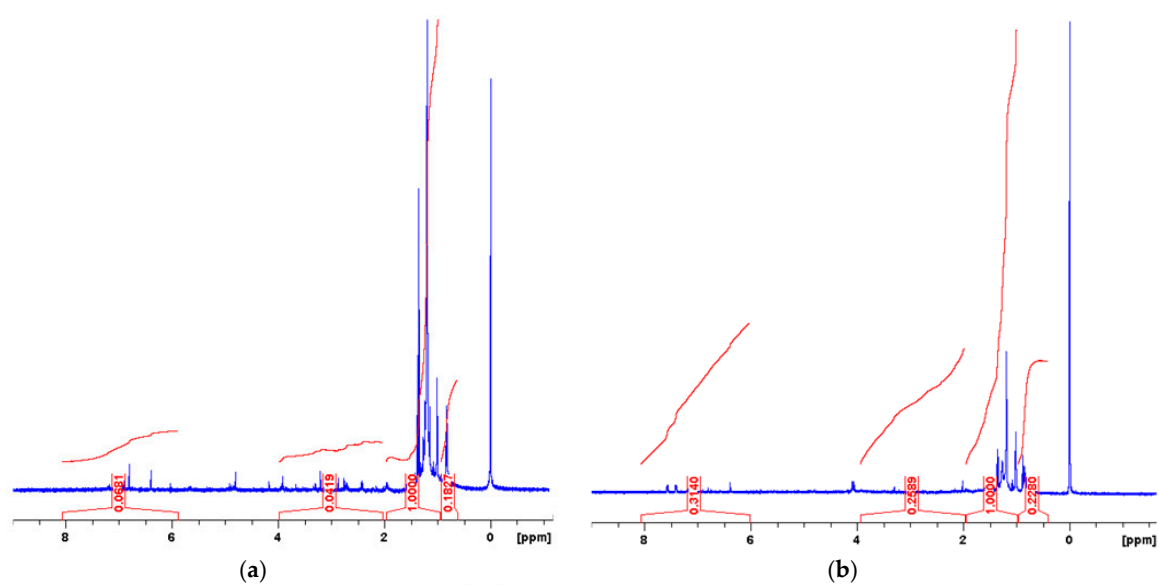
  

Bitumen	Hydrogen Distribution of Zone A $\pm 0.05$				Hydrogen Distribution of Zones B + A $\pm 0.05$			
	$H_{\text{ar}}$	$H_{\alpha}$	$H_{\beta}$	$H_{\gamma}$	$H_{\text{ar}}$	$H_{\text{ol}}/H_{\alpha}$	$H_{\beta}$	$H_{\gamma}$
Paving70/100	17.43	14.38	55.53	12.66	19.17	17.69	52.27	10.57
Paving 160/220	5.27	3.24	77.36	14.13	18.73	7.59	61.64	12.03
Industrial 160/220	6.07	8.23	71.86	13.84	-	-	-	-

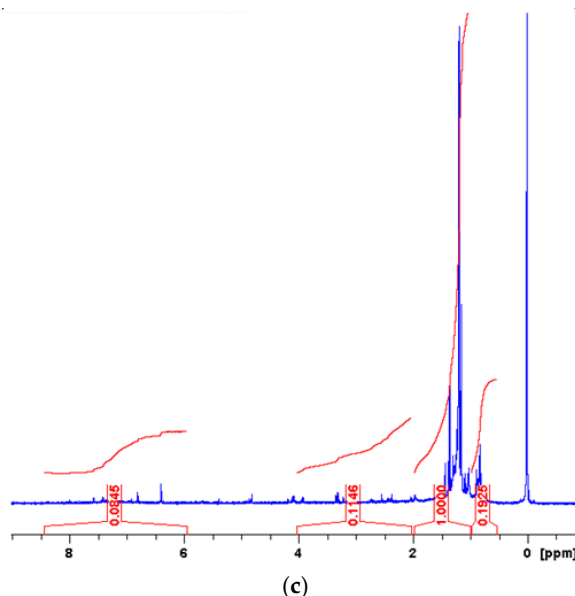
**Figure 7.** The  $^1\text{H}$ -NMR spectra of zone C obtained through a preparative TLC for the three bitumens: (a) paving 160/220; (b) paving 70/100; and (c) industrial 160/220.



**Figure 8.** The  $^1\text{H}$ -NMR spectra of zone B obtained through a preparative TLC for the three bitumens: (a) paving 160/220; (b) paving 70/100; and (c) industrial 160/220.



**Figure 9.** Cont.



**Figure 9.** The  $^1\text{H}$ -NMR spectra of zone A obtained through a preparative TLC for the three bitumens: (a) paving 160/220; (b) paving 70/100; and (c) industrial 160/220.

In the last zone A (the lower spot), the samples of the bitumen with the same grade showed a similar distribution of hydrogen, with the aliphatic part predominating with respect to the aromatic part, while the sample of the 70/100 bitumen is characterized by a higher percentage of aromatics than the others. It should be noted that, in Table 5, the distribution of  $H_{ar}$  and  $H_{ol}/H_{\alpha}$  hydrogen of zone B for the industrial bitumen is not reported. The reason for the missing data is due to an  $^1\text{H}$  experimental spectrum of this zone that does not present significant signals for these hydrogens. Important information can be extracted from Table 5; once again, the paving bitumen is poor in aromatic hydrogens and this lack can be found in both the maltene and resins. The NMR data suggest adding aromatic oils and aromatic surfactant-based mixtures to the paving bitumen to have chemical affinity similar to the industrial bitumen. This chemical affinity is very important for practical applications, e.g., solubility of polymers additives.

## 5. Conclusions and Remarks

The need for deeper insights into the characterization of bituminous materials used in industrial and infrastructural applications cast the basis for the presented research. Beyond the traditional rheo-mechanical analysis of bitumens, a deeper characterization is needed for today's multi-functional products introduced in both industry and road infrastructures. In this research, it was shown that the combined use of TLC technique and  $^1\text{H}$ -NMR spectroscopy is a feasible approach to distinguish between different bitumens even with similar physical and rheological properties.

In light of the presented achievements, the following conclusions can be made:

- Asphaltene and maltene fractions of bitumens can be successfully separated by means of TLC techniques and be used for further characterization tests in the laboratory.
- The choice of solvents determination, mobile phases and support material are crucial to obtain a consistent separation of the binder components.
- $^1\text{H}$ -NMR provides a wider perspective on the chemical characteristics of the various binders than traditional SARA analysis.
- Although within the proposed technique unconventional laboratory work is required, the obtained data provide a comprehensive understanding on the chemo-mechanical nature of the binders.

- The acquired knowledge will be at the basis of any prospective alteration/modification of binders for commercial purposes.

The described general findings are based on the laboratory study reported in this paper. Any other investigation into the use of coupled TLC and  $^1\text{H}$ -NMR methodologies may differ with changes in the bituminous material's characteristics. A consistent database should be created and disseminated for further scientific upgrades.

**Author Contributions:** All authors contributed equally to this work.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Asphalt Institute. *Superpave Asphalt Binder Specification (SP-1)*, 3rd ed.; Asphalt Institute: Lexington, KY, USA, 2003.
2. Read, J.; Whiteoak, D. *The Shell Bitumen Handbook*, 5th ed.; Thomas Telford Publishing: London, UK, 2003.
3. Handle, F.; Harir, M.; Fussl, J.; Koyun, A.N.; Grosseegger, D.; Hertkorn, N.; Eberhardsteiner, L.; Hofko, B.; Hospodka, M.; Blab, R.; et al. Tracking Aging of Bitumen and Its Saturate, Aromatic, Resin, and Asphaltene Fractions Using High-Field Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2017**, *31*, 4771–4779. [[CrossRef](#)]
4. Robertson, R.E. *Chemical Properties of Asphalts and Their Relationship to Pavement Performance*; Strategic Highway Research Program National Research Council: Washington, DC, USA, 1991.
5. Gentile, L.; Filippelli, L.; Oliviero Rossi, C.; Baldino, N.; Ranieri, G.A. Rheological and H-NMR Spin-Spin relaxation time for the evaluation of the effects of PPA addition on bitumen. *Mol. Cryst. Liq. Cryst.* **2012**, *558*, 54–63. [[CrossRef](#)]
6. Baldino, N.; Gabriele, D.; Oliviero Rossi, C.; Seta, L.; Lupi, F.R.; Caputo, P.; Falvo, T. Rheological effects on bitumen of polyphosphoric acid (PPA) addition. *Constr. Build. Mater.* **2013**, *40*, 397–404. [[CrossRef](#)]
7. Masson, J.-F.; Leblond, V.; Margeson, J. Bitumen morphologies by phase-detection atomic force microscopy. *J. Microsc.* **2006**, *221*, 17–29. [[CrossRef](#)] [[PubMed](#)]
8. Nciri, N.; Song, S.; Kim, N.; Cho, N. Chemical Characterization of Gilsonite Bitumen. *J. Pet. Environ. Biotechnol.* **2014**, *5*, 1000193. [[CrossRef](#)]
9. Aroulanda, C.; Celebre, G.; De Luca, G.; Longeri, M. Molecular ordering and structure of quasi-spherical solutes by liquid crystal NMR and Monte Carlo simulations: The case of norbornadiene. *J. Phys. Chem. B* **2006**, *110*, 10485–10496. [[CrossRef](#)] [[PubMed](#)]
10. Celebre, G.; Concistrè, M.; De Luca, G.; Longeri, M.; Pileio, G. Intrinsic information content of NMR dipolar couplings: A conformational investigation of 1,3-butadiene in a nematic phase. *ChemPhysChem* **2006**, *7*, 1930–1943. [[CrossRef](#)] [[PubMed](#)]
11. De Luca, G.; Longeri, M.; Pileio, G.; Lantto, P. NMR spectroscopy investigation of the cooperative nature of the internal rotational motions in acetophenone. *ChemPhysChem* **2005**, *6*, 2086–2098. [[CrossRef](#)] [[PubMed](#)]
12. Maltsev, A.S.; Grishaev, A.; Roche, J.; Zasloff, M.; Bax, A. Improved Cross Validation of a Static Ubiquitin Structure Derived from High Precision Residual Dipolar Couplings Measured in a Drug-Based Liquid Crystalline Phase. *J. Am. Chem. Soc.* **2014**, *136*, 3752–3755. [[CrossRef](#)] [[PubMed](#)]
13. Majid, A.; Pihillagawa, I. Potential of NMR spectroscopy in the characterization of non-conventional oils. *J. Fuels* **2014**, 390261. [[CrossRef](#)]
14. Nciri, N.; Kim, N.; Cho, N. New insights into the effects of styrene-butadiene-styrene polymer modifier on the structure, properties, and performance of asphalt binder: The case of AP-5 asphalt and solvent deasphalting pitch. *Mater. Chem. Phys.* **2017**, *193*, 477–495. [[CrossRef](#)]
15. Poveda, J.; Molina, D.; Pantoja-Agreda, E.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR structural characterization of Asphaltenes from vacuum residua modified by Thermal cracking. *J. Oil Gas Altern. Energy Sources* **2014**, *5*, 49–60. [[CrossRef](#)]
16. Maiuolo, L.; Bortolini, O.; De Nino, A.; Russo, B.; Gavioli, R.; Sforza, F. Modified N,O-Nucleosides: Design, Synthesis, and Anti-tumour Activity. *Aust. J. Chem.* **2014**, *67*, 670–674. [[CrossRef](#)]
17. De Nino, A.; Bortolini, O.; Maiuolo, L.; Garofalo, A.; Russo, B.; Sindona, G. A sustainable procedure for highly enantioselective organocatalyzed Diels-Alder cycloadditions in homogeneous ionic liquid/water phase. *Tetrahedron Lett.* **2011**, *52*, 1415–1417. [[CrossRef](#)]

18. Lee, H.-J.; Koung, F.-P.; Kwon, K.-R.; Kang, D.-I.; Cohen, L.; Yang, P.-Y.; Yoo, H.-S. Comparative Analysis of the Bufonis Venenum by Using TLC, HPLC, and LC-MS for Different Extraction Methods. *J. Pharmacopunct.* **2012**, *15*, 52–65. [[CrossRef](#)] [[PubMed](#)]
19. Dolowy, M.; Pyka, A. Chromatographic Methods in the Separation of Long-Chain Mono- and Polyunsaturated Fatty Acids. *J. Chem.* **2015**, 120830. [[CrossRef](#)]
20. Masson, J.-F.; Price, T.; Collins, P. Dynamics of bitumen fractions by Thin-Layer Chromatography/Flame Ionization detection. *Energy Fuels* **2001**, *15*, 955–960. [[CrossRef](#)]
21. Dunn, K.; Chilingarian, G.V.; Yen, T.F. *Bitumens: Liquid Chromatography*; Academic Press: Cambridge, MA, USA, 2000.
22. Christopher, J.; Sarpal, A.S.; Kapur, G.S.; Krishna, A.; Tyagi, B.R.; Jain, M.C.; Jain, S.K.; Bhatnagar, A.K. Chemical structure of bitumen-derived asphaltenes by nuclear magnetic resonance spectroscopy and X-ray diffractometry. *Fuel* **1996**, *75*, 999–1008. [[CrossRef](#)]
23. Oyekunle, L.O. Certain Relationships between Chemical Composition and Properties of Petroleum Asphalts from Different Origin. *Oil Gas Sci. Technol. Rev. IFP* **2006**, *61*, 433–441. [[CrossRef](#)]
24. Preethi, J.; Harita, B.; Rajesh, T. Review on Thin Layer Chromatography. *J. Formul. Sci. Bioavailab.* **2017**, *1*, 1–4.
25. Zander, M.; Marsh, H.; Rodríguez-Reinoso, F. Chemistry and properties of coal-tar and petroleum pitch. In *Sciences of Carbon Materials*; Marsh, H., Rodríguez-Reinoso, F., Eds.; Universidad de Alicante, Secretariado de Publicaciones: Alicante, Spain, 2000; pp. 205–257.
26. Çubuk, M.; Gürü, M.; Kürşat Çubuk, M. Improvement of bitumen performance with epoxy resin. *Fuel* **2009**, *88*, 1324–1328. [[CrossRef](#)]



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